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Stochastic Search for Isomers of the *sec*-Butyl Cation

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Abstract: A stochastic search procedure for locating energy minimum structures was applied to the *sec*-butyl cation. A previously unreported structure **3′** with strong H-hyperconjugative stabilization of the carbocation center was found at several levels of theory (HF, B3LYP, and MP2). The theoretical equilibrium isotope effect (EIE) for the monodeutero isotopomer of **3′** ($K_{eq} = 1.4$; $t = -130$ °C) indicates that the new structure is likely to be largely responsible for the experimentally observed EIE.

Introduction

Only three simple secondary carbocations have been prepared in stable solution. The isopropyl,[1] *sec*-butyl,[2] and cyclopentyl[3] cations have all yielded valuable and novel information about carbocation rearrangement processes through experimental observations. The isopropyl cation has a basically classical structure with NMR signals for the inside carbon and hydrogen shifted far downfield. These chemical shifts are close to those predicted by current quantum mechanics programs for the bare carbocation. The inside C and H can be shown to exchange with the methyl carbons and hydrogens by the NMR line shape method and also by isotopic labeling, in both cases yielding rates and barriers. Although the first mechanism suggested began with an uphill 1,2 hydride shift to the primary *n*-propyl cation, no minimum has been found on the energy surface near this structure. The experimental data are consistent with a mechanism involving going over a transition state to a protonated-cyclopropane intermediate.[1]

The cyclopentyl cation shows a single sharp NMR signal for the carbons and a single line for the protons even at very low temperatures.[3] This is evidence for extraordinarily rapid hydrogen shifts over low barriers. However, it can be demonstrated that carbon scrambling in this ion has a high barrier. The 1,2 and 1,3 di-^{13}C-labeled cations give distinct CMR signals and do not interconvert up to the stability limit of the cation. In addition, no conversion to the isomeric methylcyclobutyl cation can be detected even though this cation can be independently prepared and is also stable. It is striking that many attempts to prepare the cyclohexyl cation have failed and have resulted only in the formation of the methylcyclopentyl cation.[4]

The *sec*-butyl cation is probably the most interesting of the three. The *sec*-butyl cation was first examined experimentally in a superacid solution at low temperatures (below −100 °C)[2,5] and later in the solid state.[6] ^{13}C NMR and ^{1}H NMR spectra show that the two methyls are very rapidly interconverted. The inside carbons give a single averaged peak as do the three inside hydrogens. This **must** be due to a rapid process since no structure has been suggested which makes the three inside hydrogens equivalent. The barrier must be extremely low since no line-broadening has been seen at very low temperatures in solution. Even studying the ion in the solid state at temperatures close to 0 K has shown no sign of slowing this process.

It can be demonstrated that the inside and outside hydrogens and inside and outside carbons interchange rapidly enough in the stability range for this cation via line shape and isotopic labeling methods. However, even though ^{13}C can go back and forth between the inside and outside, not all isotopomers are in equilibrium. Three of the four di-^{13}C-labeled ions interconvert, but the fourth one is unchanged over time. This striking result follows directly from the protonated-cyclopropane mechanism which had been proposed for this rearrangement.[2c]

Examining the NMR chemical shifts (experimental and calculated) and monitoring rearrangements has given us much information about these ions but, fortunately, does not

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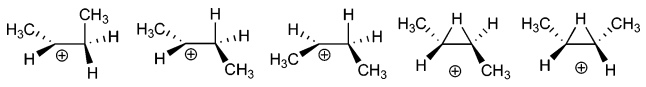
exhaust our methodology. When there are degenerate and rapid rearrangements, introduction of the isotopes so as to break the degeneracy often produces a substantial splitting in the averaged peaks. This procedure, called the isotopic perturbation method, has been applied to many carbocations (and also to non-carbocation cases).[7] The 2,3-dimethylbutyl cation yields very large and temperature-dependent splittings as a result of introducing deuterium. This perturbs a rapid rearrangement process involving a degenerate hydride shift.[8] Quantum mechanical calculation of the Cartesian force constant matrix for an optimized structure for this ion, followed by application of the program QUIVER,[9] allowed prediction of the equilibrium isotope effects (EIEs) for a large number of deuterated isotopomers for this ion. This enabled an accurate fitting of the splittings in the CMR spectrum. In the norbornyl cation, deuteration induces no observable splitting. This is one of the strongest pieces of evidence for the symmetrically bridged (nonclassical) structure for this ion.

In the *sec*-butyl cation, structures with deuterium on a methyl show substantial splitting in the ^{13}C NMR spectrum of the inside carbons. The unusual feature of the splitting is that it becomes larger at higher temperature (10.85 ppm at −134 °C, 10.95 ppm at −130 °C, and 11.02 ppm at −126 °C, respectively). This suggests that at least two different structures exist in solution and that the structure having higher energy induces a larger splitting. The presence of several different minimum-energy structures makes accounting for this splitting both challenging and interesting.

Quantum chemical calculations have been done in the past at the HF/6-31G(d) level on the partially bridged structure **1** with strong C-hyperconjugation and on the open-chain form **2** with H-hyperconjugative stabilization (methyl groups in the trans relation).[10] The open-chain form **3** with methyl groups in the cis relation (C_s symmetry) was located as a transition-state structure. At theoretical levels including electron correlation [MP2(full)/6-31G(d) level, four minima were found: **1**, **2**, and the two symmetrically hydrido-bridged forms **4** and **5** in which methyl groups are in the trans or cis position, respectively. However, isomer **2** refined into a bridged structure **4** when a larger basis set [6-311G(d,p)] was used.[10a]



1 **2** **3** **4** **5**

Since only structure **1** of all located minimum energy structures undergoes rapid equilibrium interchanging the hydrogen, we calculated the equilibrium isotope effect at −130 °C (experimental temperature) that would produce **1**, using the program QUIVER,[9] and obtained $K_{eq} = 1.005$. Such a small effect would split the central carbons less than 1 ppm (vs 11 ppm in the experiment). Therefore, it was apparent that a fraction of 2-butyl cations must exist in a form that had not yet been theoretically located on the potential energy surface (PES). At least one additional structure must be responsible for the observed large EIE.

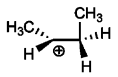
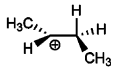
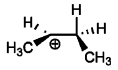
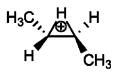
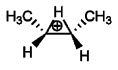
It is highly desirable to locate all of the accessible minimum-energy structures in order to account for experimental results theoretically. Until recently, chemists entered all of the approximate structures that they could think of and then refined each of them using quantum mechanics calculations. Calculations could be done at higher and higher levels in attempting to obtain accurate results. However, if a structure close to one of the minima on the energy surface is not thought of, it will not be found using this procedure. For common molecules with well-defined bonds, it is relatively easy to suggest all of the possible structures. However, carbocations can have fractional bonds of various orders and very unusual geometries. For the *sec*-butyl cation, the known energy surface is so rich that one must be very concerned about the problem of finding all of the important minima. Fortunately, a stochastic search procedure for locating all the isomers on an energy surface defined by quantum chemical calculations has been described recently.[11,12] The method is analogous to the stochastic random search procedure for finding conformers previously developed and extensively used for molecular mechanics surfaces.[13] An important feature of these two methods is that intensive enough application is virtually certain to find all of the structures. In applying this method, a starting structure is subjected to a "kick", which moves each atom in a random direction over a random distance within a sphere of given radius (R), which represent the maximal kick size. Optimization of the kicked structure with a quantum mechanical optimizer could take it back to the initial structure, or it can be refined to give a different isomer. To imagine that there is some minimum which **cannot** be found using this method even with a very large number of kicks, one must conceive of a structure which cannot possibly be produced by a kick. This is hard to imagine. Quantum mechanical calculations can be done at many levels. It is possible that a structure which is a minimum at one level is not a minimum at another level. In principle, stochastic searches could be carried out at all levels, but the computer time required would be very large. A way of improving the likelihood that one has found all minima is to use each of the found minima in turn as the starting point for a new search. If each minimum yields all of the other known minima, that is an encouraging sign.

We applied the stochastic search procedure on the PES of the 2-butyl cation to seek additional structures. We first applied it at the HF level of theory, and then also at B3LYP and MP2 levels.

Results and Discussion

Stochastic Search Procedure at HF Levels. Five different 2-butyl cation isomers were used as initial structures for the stochastic kick procedure at the HF/6-31G(d) level (Table 1): the open-chain forms **1** (C_1 point group, NImag = 0), **2** (C_1 point group, NImag = 0), and **3** (C_s point group, NImag = 1) and the two hydrido-bridged forms **4** (C_2 point group, NImag = 1) and **5** (C_s point group, NImag = 1). The protonated methylcyclopropane **6** (C_1 point group, NImag = 0) was also used as the initial structure in this procedure. Each $C_4H_9^+$ isomer was kicked systematically with kicks ranging from 0.7 to 1.1 Å. It has been found that the convergence failure or fragmentation of the initial structures occurred frequently during optimization if kicks larger than

Table 1. Relative Energies of Structures **1**−**9** Found by the Stochastic Search Method Performed at the HF, DFT, and MP2 Levels

Structures located by stochastic search method	ΔE/kcal mol^{-1} [a]			
	HF/6-31G(d)	B3LYP6-31G(d)	MP2(FU)/6-31G(d)	CCD/6-311G(d,p)[b]
 **1**	0	0	0	0
 **2**	-0.4	-0.2	2.0	-
 **3'**	0.1	-0.1	2.3	0.3
 **4**	-	1.0 [c]	1.2	-1.0
 **5**	-	1.9 [d]	2.1	-0.03
6	14.8	11.7	8.1	8.2
7	-14.7	-14.9	-12.9	-14.1
8	-	-	48.5	43.3
9	-	-	46.6	41.3

[a] Relative energies including ZPE corrections. [b] CCD geometry optimization of the corresponding MP2 structures found by stochastic search. [c] First-order saddle point; NImag = 1 (−126; hydride shift). [d] First-order saddle point; NImag = 1 (−180; hydride shift).

1.1 Å were applied. The range of kick sizes between 0.8 and 0.9 Å was found to be optimal for the stochastic search here. Optimizations of kicked structures were easily completed and led to stationary points, and only relatively few fragmentations occurred.

By using the stochastic search method, the additional minimum **3′** (cis isomer) was discovered (Figure 1). The open-chain form **3′** (C_1 point group, NImag = 0) is the CH-hyperconjugative isomer and is similar in geometry to the symmetrical transition structure **3** (C_s point group, NImag = 1) reported previously. The isomer **3′** is stabilized by 2-fold hyperconjugative interaction between C1−H and C3−H bonds and the formally empty 2p orbital at the C2 carbon atom. These C−H bonds are elongated (1.101 and 1.103 Å, respectively).

It has been found that, regardless which of the initial structures **1**−**6** has been used for stochastic search, all other $C_4H_9^+$ isomers could be located, including structure **3′**. In addition to 2-butyl cation isomers (**1**, **2**, and **3′**) and to protonated methylcyclopropane (**6**), the *tert*-butyl cation (**7**) was also located no matter which starting structure for a search was used. Therefore, every starting structure converged to every other isomer easily, indicating a high probability for the corresponding isomerization. The exception is the *tert*-butyl cation (**7**), which, when used as a starting point for a search, fell back to the initial structure if the optimization converged successfully. The *tert*-butyl cation is much lower in energy and far removed in structure space from all of the *sec*-butyl structures discussed here.

As mentioned above, by applying kicks larger than 1.1 Å, fragmentation of the molecule often occurs. These fragmentation results are interesting since they can be compared with both experimental and theoretical studies of the carbocation rearrangements and carbocation dissociation chemistry.[14] For example, it is shown that metastable $C_4H_9^+$ ions dissociate by the loss of methane or ethene, yielding the fragment 2-propenyl ion $CH_3C^+CH_2$ or the nonclassical $C_2H_5^+$ ion, respectively.[15] These types of dissociation processes observed experimentally in the gas phase were "reproduced" during the geometry optimization of the

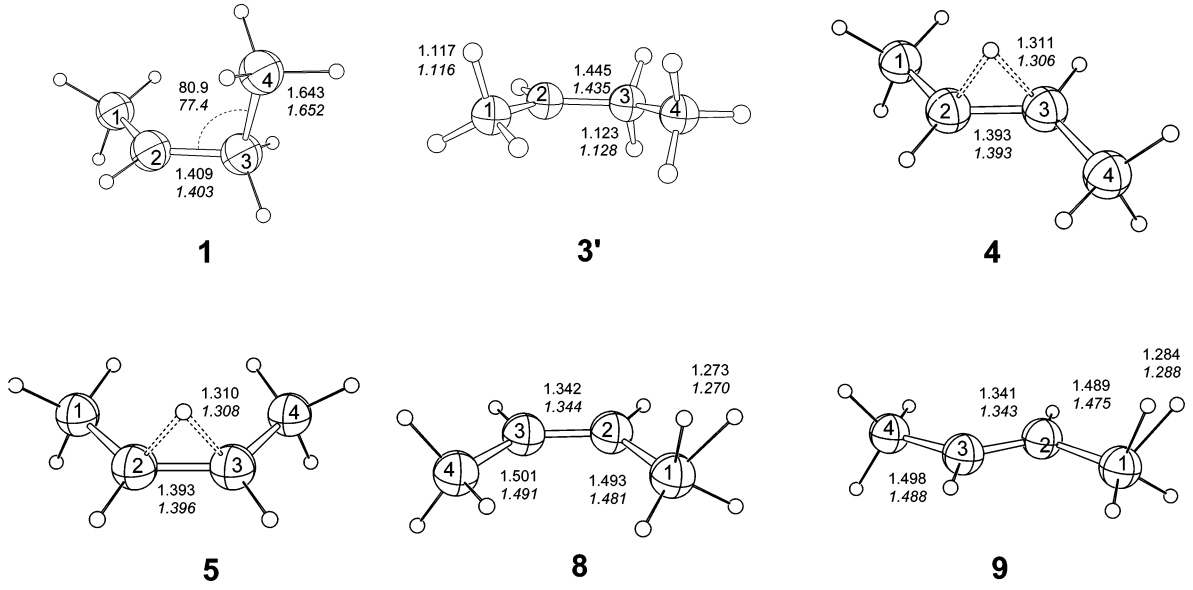


Figure 1. CCD/6-311G(d,p) optimized structures of the 2-butyl cation isomers **1**−**9** located at the $C_4H_9^+$ PES using the stochastic search method at the MP2(full)/6-31G(d) level (MP2 geometry parameters are in italics). Bond distances are in angstroms; bond angles are in degrees.

corresponding kicked structures. In addition to the elimination of methane and ethene, several geometry optimizations completed with the ethane, carbene CH_2 (yielding the isopropyl cation), or H_2 eliminations.

Stochastic Search Procedure at MP2 and Density Functional Theory (DFT) Levels. The stochastic search procedure for $C_4H_9^+$ isomers was repeated at the MP2(full)/6-31G(d) level of theory, using the same kicked input as for the procedure at the HF/6-31G(d) level. Several new minima, not observed at the HF/6-31G(d) level, were located. Along with structures **1**, **2**, **6**, and **7**, the two hydrido-bridged trans (**4**) and cis (**5**) forms were found to be minima (Figure 1), which is in agreement with earlier computational studies.[10a] The open-chain form **3′**, not reported in earlier studies as a minimum at the MP2 level, was located as well. We feel that this structure is likely to be the "missing structure" that is required to account for the experimentally measured equilibrium isotope effect.

Some unusual and unstable (ca. 40 kcal/mol less stable than **1**) $C_4H_9^+$ structures were also discovered this way (Figure 1), such as the methyl-protonated *cis*-butene (**8**) and *trans*-butene (**9**). These two structures are related to studies on the acid-catalyzed isomerization and rearrangements of *n*-butane and 2-butene.[16]

Again, it was found that, by using initial structures **1**−**6** for the stochastic search at the MP2 level, and kicks ranging from 0.7 to 1.1 Å, all other $C_4H_9^+$ isomers (**1**−**7**) were located. If the *tert*-butyl cation (**7**) was used as an input structure for the stochastic search, the kicking procedure and the subsequent geometry optimization of the corresponding kicked structure always returned to **7**. In comparison with the HF/6-31G(d) level of theory, the number of convergence failures or fragmentations of the initial structures during the geometry optimizations was reduced when the MP2/6-31G(d) level was employed (Table 2). The reason that relatively few structures converged to the *tert*-butyl cation if any of the $C_4H_9^+$ structure was used as an initial structure is due to the relatively small kick size applied.

Table 2. Results of the Stochastic Search Performed by Subjecting the Input Structure **3** to 50 Kicks and Optimizing the Kicked Structures at Different Levels of Theory[a,b]

HF/6-31G(d)[c,d]	B3YLP/6-31G(d)[c,d]	MP2(FU)/6-31G(d)[c,d]
3′ (26)	**3′** (30)	**3′** (24)
6 (2)	**1** (2)	**1** (2)
7 (2)	**6** (2)	**6** (2)
X (20)	**7** (2)	**7** (2)
	X (14)	**5** (8)
		4 (2)
		8 (2)
		X (8)

[a] Initial structure **3** was perturbed by a kick of 0.8 Å. [b] Route section: Opt = Tight, Freq, IOP(5/13 = 1). [c] The bold number represents the energy minimum structure obtained by geometry optimization of the kicked structure; the number in parentheses corresponds to the number of optimization procedures that converged to a given minimum (out of 50 kicks). [d] **X** represents any fragmentation or convergence failure during a geometry optimization procedure.

Overall, five 2-butyl cation structures (**1**, **2**, **3′**, **4**, and **5**) were located as minima at the MP2(full)/6-31G(d) level, and their relative energies are presented in Table 1. The new minimum **3′**, not reported previously, was found to be the least stable isomer, that is, 4.0 kcal/mol less stable than the partially methyl-bridged structure **1** [0.9 kcal/mol at the HF/6-31G(d) level]. The isomer **3′** is, similarly as on the HF level, characterized by 2-fold hyperconjugative interaction between C1−H and C3−H bonds and the formally empty 2p orbital at the C2 carbon atom.

The results obtained from the stochastic search at the HF/6-31G(d) and MP2(full)/6-31G(d) levels were compared to those obtained with the B3LYP/6-31G(d) method (Tables 1 and 2). Again, three different minima (**1**, **2**, and **3′**) of the 2-butyl cation were discovered using the stochastic method at the DFT level. At the B3LYP/6-31G(d) level, the two

H-bridged trans (**4**) and cis (**5**) forms, found to be minima at the MP2/6-31G(d) level, were located as transition states for the 1,2-hydride shift in **2** and **3′**, respectively. The stochastic methodology might be also applied in searching for the transition states on an energy surface. However, as was stated before,[11] a complete search for transition state structures would take much more computer time (many more kicks needed to find them all).

Once the energy minimum structures were located at the MP2(full)/6-31G(d) level, the results were refined by calculations performed at higher levels of theory. All stationary points located by the stochastic search method at the MP2-(FU)/6-31G(d) level were subjected to optimization and frequency calculation at the CCD/6-311G(d,p) level of theory (Table 1). At this level of theory, structure **2** vanished from the $C_4H_9^+$ PES and converged to hydrido-bridged structure **4**. The same was observed at the MP2/6-311G(d,p) and CCD/6-311G(d,p) levels of theory by Schleyer et al.,[17] which suggests that structure **2** cannot be characterized as a minimum. In order to verify that structure **3′** is a real minimum at the PES, its structure was optimized using the larger basis set [6-311G(d,p)] at levels which provide a more sophisticated treatment of electron correlation: MP*n*, CCD, and QCISD. Similarly as with structure **2**, at the MP2/6-311G(d,p) and MP3/6-311G(d,p) levels, structure **3′** converged to hydrido-bridged structure **5**. However, at the MP4(SDQ)/6-311G(d,p) and CCD/6-311G(d,p) levels of theory, open-chain energy minimum structure **3′** with strong H-hyperconjugation was located. At the former level, it was confirmed that structure **3′** is a minimum; that is, all calculated frequencies were real. The same result was obtained at the CCD level of theory with an extended basis set, 6-311++G(d,p), which includes additional diffusion functions on both carbon and hydrogen atoms. Finally, the QCISD level of theory, which represents a more sophisticated method for the treatment of electron correlation beyond MP4 (and usually providing even greater accuracy), was used for the optimization of structure **3′**. No conversion to the hydrido-bridged structure was observed upon geometry optimization. Therefore, it can be concluded that four different minima (not including structures **8** and **9**) exist on the 2-butyl cation PES: a CC-hyperconjugatively stabilized isomer **1**, a 2-fold CH-hyperconjugatively stabilized isomer **3′**, and two hydrido-bridged structures **4** and **5**. At the CCD/6-311G(d,p) level, hydrido-bridged structure **4** is calculated to be the most stable isomer, but the energies of **1**, **3**, and **5** are in the very narrow range of only 0.3 kcal/mol.

It is important to emphasize again that each of the input structures (**1**−**6**) converged to all energy minimum structures (**1**−**7**), which indicates the reliability of the method. The big advantage of the stochastic method is that it is very much less likely to miss structures than the "classical method" in which reasonable guessed starting geometries are used as an input in searching for the structures.

In order to carry out the stochastic search effectively, attention should be focused on the following points:

1. The range of kick size between 0.8 and 0.9 Å is optimal for this stochastic search; that is, most of the optimizations of kicked structures were completed, and only a few fragmentations occurred. In this kick size range, the fewest kickings are required to discover all the isomers.

2. The efficiency of the optimization of the kicked structures depends on the choice of the coordinate system. Redundant internal coordinates were the best choice for optimizing initial structures.

3. Convergence- and algorithm-related options could be more important to implement when doing stochastic searches on larger molecular systems. It is found that, when the size of the kicked structure is large, the number of convergence failures and fragmentations will increase.

4. Electron-correlated methods, such as MP2, seem to be more effective than HF methods in searching for new isomers.

5. The results of the stochastic search at the DFT level are dependent on the numerical integration grid used in calculations. The number of steps for geometry optimization and the number of imaginary frequencies of isomers located are affected if different grid sizes are applied in DFT calculations.

Equilibrium Isotope Effect of the 2-Butyl Cation. As mentioned above, a new structure **3′** was found to be a minimum at all levels of theory. In order to find out whether the monodeuterated isotopomer of **3′** (one deuterium on the methyl group) can produce splitting of the central carbon in ^{13}C NMR that is in accord with the experimental findings, we calculated the EIE with the program QUIVER[9] using the geometry optimized at the MP2(FU)/6-31G(d) level and obtained $K_{eq} = 1.396$ (at −130 °C). When the equation $K_{eq} = (\Delta + \delta)/(\Delta - \delta)$ was used, in which K_{eq} is the equilibrium constant of interchange of the hydrogen between C2 and C3 in the monodeuterated isotopomer, Δ is the chemical shift difference between C2 and C3 carbons in the static carbocation,[18] and δ is the splitting caused by deuterium,[19] it was predicted that the central carbons in the ^{13}C NMR spectrum of pure **3′** at −130 °C should be split by 41 ppm. Because of the very flat surface, all four established isomers (**1**, **3′**, **4**, and **5**) interconvert over very low barriers, so the net splitting of the central carbon atoms reflects the weighted average contribution of all structures. Since only **3′** produces considerable splitting of the central carbons, it is expected that the observed splitting will be smaller than that calculated for the pure isomer **3′**. This is in accord with the experimental result (ca. 11 ppm). Experimental observations that the splitting of the central carbons increases at higher temperatures are consistent with theoretical results according to which isomer **3′** is the highest-energy structure of all energy minimum structures of the 2-butyl cation. Therefore, isomer **3′** is indeed likely to be the previously "missing" energy minimum structure on the PES of the 2-butyl cation that is largely responsible for the observed EIE.

Computational Methods

The quantum chemical calculations were performed using the Gaussian 98 program suite.[20] All structures were fully optimized using the DFT method (B3LYP) or ab initio methods, (Hartree−Fock, Møller-Plesset perturbation theory, and coupled cluster calculation). The MP2 calculations were performed using the Full option (all electrons included in

the correlation calculation), while coupled cluster calculations were performed using double substitutions from the Hartree−Fock determinant (CCD). The standard split valence and polarized 6-31G(d) basis set was employed in the geometry optimizations and frequency calculations. For comparison, we also carried out calculations with the larger basis set 6-311G(d,p). A vibrational analysis was performed at the same level of theory in order to determine the zero-point vibrational energy (ZPE) and to characterize each stationary point as a minimum (NImag = 0) or transition state structure (NImag = 1). The optimized MP2/6-31G(d) geometries were subjected to geometry optimization and frequency calculations at the CCD/6-311G(d,p) level. Corrections for ZPE (not scaled) are included in the calculated energies. The relative energies are given in kilocalories per mole with respect to the 2-butyl cation isomer **1** and are listed in Table 1.

For comparison, a job completed (geometry optimization successfully converged to one of the isomers) in 70 steps using the HF/6-31G(d) method requires 43 min (RWF = 6 MB), whereas corresponding jobs using the MP2(full)/6-31G(d) or B3LYP/6-31G(d) method require 130 (RWF = 10 MB) or 216 min (RWF = 10 MB), respectively. Frequency calculations at corresponding levels require 4.5 (RWF = 15 MB), 20 (RWF = 299 MB), and 25 (RWF = 15 MB) minutes, respectively. All these calculations were performed as single-processor jobs on a Linux computer with mem = 256 MB and maxdisk = 2000 MB options.

Details of the Stochastic Search at the HF Level. To check whether the results of these isomerizations depend on the coordinates in which structures are optimized (redundant internal coordinates were used as a default), we repeated the geometry optimizations of the kicked structures (with the same input) using Cartesian and internal coordinates (Z matrices). In some cases, the geometry optimization of the kicked structure gave different results when performed in a different coordinate system. For example, the optimization of the initial *cis*-2-butyl cation structure (**3** kicked by 0.8 Å) converged to isomer **1** when using redundant internal coordinates; structure **3′** was obtained when using Cartesian coordinates, and the minimization failed (the CH_2 fragment was "eliminated" and the isopropyl cation formed) when using internal coordinates (Z matrices). In general, the overall results of the stochastic search for $C_4H_9^+$ isomers were quite similar regardless to the coordinate system used in the optimization procedure. The same pattern that one isomer gives all others was observed when optimizations of the kicked structures were carried out in the model solvent (ϵ = 78.4 and a_0 = 4.0 Å) using the Onsager reaction field model (self-consistent reaction field = dipole) at the HF/6-31G(d) level of theory. As expected,[21] redundant internal coordinates were the best choice for optimizing these kicked geometries. The number of steps required to fully optimize kicked geometries was the lowest when redundant internal coordinates were used. Cartesian coordinates were shown to be superior to internal coordinates (Z matrices). This is probably because programs (Gaussview, Molden, or NewZMat utility in Gaussian), which can generate a Z matrix automatically from other coordinates, make a poorly constructed Z matrix for atypical (kicked) geometries.[22]

The efficiency of the optimization in redundant internal coordinates could also be improved by the Expert option ("OPT = Expert" keyword in the input route section). It is a convergence-related option which relaxes various limits on maximum and minimum force constants and step sizes enforced by the Berny program.[23] It is useful in cases where the forces and force constants are very different from those of typical molecules such as in kicked structures. In our case, this option led to faster convergence and decreased the number of optimization steps. It can be used in conjunction with an option (CalcFC) which specifies that the force constants be computed at the first point.

Algorithm-related options (Steep, GDIIS, and the quadratically convergent SCF procedure) were also tested, but only minor effects were observed. However, these convergence- and algorithm-related options might be more important if implemented in stochastic searches on larger molecular systems. It is likely that if the kick size is larger, the number of convergence failures and fragmentations (which cannot be foreseen from the initial kicked input) will also increase. In the case of simple models reported previously,[11,12] no elimination of small molecules occurred, whereas in the case of the $C_4H_9^+$ system, such fragmentations were quite frequent during the optimization procedure.

If the stochastic search for $C_4H_9^+$ isomers was begun with all atoms at the origin, as described for the C_6 cluster,[11] no optimization converged at all, even though different convergence- and algorithm-related options were used. In contrast with the case of C_6 clusters, kicking the atoms-at-origin input and subsequent optimization of the kicked structure resulted in either hydrogen elimination or abnormal job termination.

Details of the Stochastic Search at MP2 Level. When the initial kicked structures (isomer **3** kicked by 0.8 Å) were optimized at the MP2 level, only eight optimization procedures failed (out of 50), whereas 20 failures occurred if the same structures were optimized at the HF level. Although more expensive,[24] electron-correlated methods, such as MP2, are more effective in searching for new isomers and more useful in describing the $C_4H_9^+$ PES via the stochastic search procedure. For example, the geometry optimization of the initial *cis*-2-butyl cation structure (**3** kicked by 0.8 Å) converged to seven different isomers (**1**, **2**, **3′**, **5**, **6**, **7**, and **8**) when using the MP2 method, whereas only three (out of five possible) different isomers (**3′**, **6**, and **7**) were located when the HF method was employed.

Details of the Stochastic Search at the DFT Level. The density functional theory was found to be less effective than the MP2 method in searching for new isomers on the $C_4H_9^+$ PES. A much larger number of kicks (with different kick sizes) is necessary to reproduce the results calculated at the MP2 level.

The efficiency of the DFT method is comparable to that of the HF method. However, the number of steps needed to complete the geometry optimization of the initial kicked structure is usually larger in the case of the B3LYP method. For example, the geometry optimization of the initial *cis*-2-butyl cation structure (**3** kicked by 0.8 Å) converged to corresponding isomers (**1**, **2**, **3′**, **5**, **6**, **7**, or **8**) in ca. 50−60

steps when using the HF (or MP2) method, whereas more than 100 steps were needed to complete the optimization procedure when the DFT method was employed. To solve this convergence problem when using the DFT method, we have tested a "loose" option which sets the optimization convergence criteria to a maximum step size of 0.01 au and an RMS force of 0.00017 au. These values are consistent with the SG1Grid grid size [IOP(5/44=1) setting] which is expected to speed up geometry optimizations, especially when still far away from the next stationary point. Although the loose option is intended only for a preliminary work, we found it useful to speed up the DFT convergence. The isomers located with the tight option were reproduced with the loose option but in a much smaller number of steps (ca. 70 steps). Smaller grids [a CoarseGrid grid size with IOP(5/44=2) setting] were also tested, but no improvement was obtained. On the contrary, all geometries obtained with a small grid size are characterized with one or more imaginary frequencies (mostly methyl rotor). This artifact is known for methods which use numerical integration of the functional, such as density functional theory, since the accuracy of this grid size is not high enough for computing low-frequency modes very precisely.

Therefore, the results of the stochastic search at the B3LYP level are dependent on the numerical integration grid used in calculations.[25] Both the number of steps for geometry optimization and the number of imaginary frequencies of isomers located are affected if different grid sizes are applied in DFT calculations.

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Supporting Information Available: Cartesian coordinates of structure **3′** optimized at the HF, MP2, and CCD levels and optimized structures **1**, **4**, **5**, **6**, **8**, and **9** at the CCD/6-311G(d,p) level. Cartesian coordinates of structure **3′** optimized at the MP4(SDQ)/6-311G(d,p), CCD/6-311++G(d,p), and QCISD/6-311G(d,p) levels are enclosed as well.

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(22) Geometry optimizations in internal coordinates (Z matrices) were often aborted with a message that "angle Alpha is outside the valid range", that is, that the conversion from Z matrix to Cartesian coordinates failed.

(23) See the Gaussian 98 User's Reference on the Web. http://www.gaussian.com/g_downloads/g98help.zip (accessed Oct 1, 2006).

(24) Frequency calculations of $C_4H_9^+$ isomers at the MP2(FU)/6−31G(d) level of theory are about 5 times slower than the corresponding calculations at the HF/6−31G-(d) level.

(25) It is important to use the *same* grid for all calculations where one intends to compare energies (e.g., computing energy differences or heats of formation).

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