# Nature of the 2-Bicyclo[3.2.1]octanyl and 2-Bicyclo[3.2.2]nonanyl Cations

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Density functional and ab initio calculations have been employed to explore the nature of the cations formed in the solvolysis of 2-bicyclo[3.2.1]octanyl tosylate the 2-bicyclo[3.2.2]nonanyl tosylate. In contrast to recent conclusions in the literature, the various proposed classical carbocations postulated to explain the products of the 2-bicyclo[3.2.2]nonanyl tosylate solvolysis were found to have nonclassical structures.

## Introduction

In the decades following World War II, studies of organic solvolysis reactions greatly increased our knowledge of carbocation processes. These studies[1] were aided by the introduction of tools such as isotopic tracers, infrared spectroscopy, and ultimately nuclear magnetic resonance spectroscopy.

In the 1960s, Goering et al.[2,3] studied the solvolysis of 2-bicyclo[2.2.2]octanyl tosylate and the *exo* and *endo* stereoisomers of 2-bicyclo[3.2.1]octanyl tosylate. The reaction rates and products were examined to establish that the two bicyclo[3.2.1] tosylates produced two different carbocations which were best described in terms of nonclassical bridged ion intermediates. The 2-bicyclo[2.2.2]octanyl tosylate and the *exo*-2-bicyclo[3.2.1]octanyl tosylate were shown to give products related to the same carbocation intermediate, and it was shown that ion pair internal return equilibrated the two starting tosylates, leading to a common product mixture.

In 1967 Shaefer, Endres, and Moran[4] reported the acetolysis of 2-bicyclo[3.2.2]nonanyl tosylate to give a mixture of the acetates derived from 2-bicyclo[3.2.2]nonanol, 3-bicyclo[3.2.2]nonanol, and *exo*-2-bicyclo[3.3.1]nonanol. The mechanism written at the time consisted of the standard Whitmore mechanism for 1,2-shifts involving carbocations with the charge localized on one carbon at a time.

In a recently published study, Okazaki et al.[5] utilized carbon-13 labeling to study the solvolysis and rearrangement of 2-bicyclo[3.2.2]nonanyl tosylate in methanol and also 2,2,2-trifluoroethanol at 50 °C. They reported the formation of the ethers derived from the 2-bicyclo[3.2.2]nonanyl and 2-bicyclo[3.3.1]nonanyl systems. They made no comment regarding the 3-bicyclo[3.2.2]nonanol structure reported by the Schaefer group.[4] The observed scrambling pattern for the isotopic carbon was rationalized on the premise that a classical carbocation 1,2-shift mechanism was in operation. One product required the proposal of a 1,3-hydride shift. Though a well-known phenomenon, the mechanistic details of such shifts are still a matter of some controversy.[6]

One method of clarifying the question of classical vs nonclassical ion intermediates or transition structures is by modern computational methodology. As an example, one may cite the recent work of Farcasiu, Norton, and Hâncu.[7]

Density functional theory (DFT) has now been applied to the structures of the 2-bicyclo[3.2.1]octanyl and the 2-bicyclo[3.2.2]nonanyl cations with the results given below.

## Computational Methods

Classical ions (Figure 2; **1, 3, 5, 8**) were optimized by AM1 calculations with single-point energies determined at the B3LYP/6-31G* level. These starting classical cations displayed signs of distortions toward the nonclassical structures even at the ab initio HF/3-21G* level. Subsequently these ions were reoptimized (B3LYP/6-31G*//B3LYP/6-31G*) employing the Gaussian 98 set of programs.[8] Structures, vibrations, and pertinent molecular orbitals were examined visually by Gaussview.[9] Stable ion structures (**2, 4, 6, 9**) were tested by frequency calculations and shown to provide all real vibrational frequencies.

The transition structure (**7**) was optimized at the B3LYP/6-31G* level and a frequency calculation performed. A single imaginary frequency was examined visually to confirm that it corresponded to a rational reaction coordinate motion.

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(1) For a review see: Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill Book Co.: New York, 1962.

(2) Goering, H. L.; Sloan, M. F. *J. Am. Chem. Soc.* **1961**, *83*, 1397, 1992.

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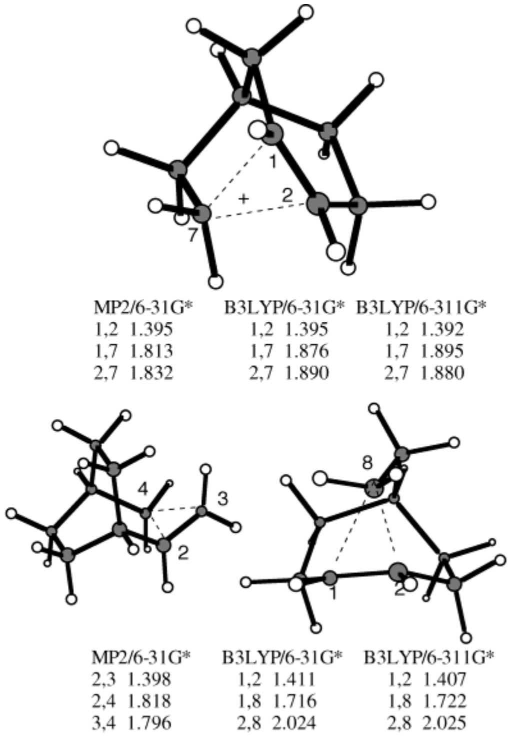
10.1021/jo0006167 CCC: $20.00



| MP2/6-31G* | B3LYP/6-31G* | B3LYP/6-311G* |
|---|---|---|
| 1,2 1.395 | 1,2 1.395 | 1,2 1.392 |
| 1,7 1.813 | 1,7 1.876 | 1,7 1.895 |
| 2,7 1.832 | 2,7 1.890 | 2,7 1.880 |

| MP2/6-31G* | B3LYP/6-31G* | B3LYP/6-311G* |
|---|---|---|
| 2,3 1.398 | 1,2 1.411 | 1,2 1.407 |
| 2,4 1.818 | 1,8 1.716 | 1,8 1.722 |
| 3,4 1.796 | 2,8 2.024 | 2,8 2.025 |

**Figure 1.** Influence of basis set choice and computational methodology on the structures of several cations in this study.

## Results and Discussion

Schleyer and co-workers[10] have demonstrated that hybrid density functional models such as B3LYP with the 6-31G* basis set give adequate levels for structure determinations where nonclassical carbocations may be important. To confirm the method, the classical 2-bicyclo-[3.2.1]octanyl and 2-bicyclo[3.2.2]nonanyl cations were optimized by two different methods. The first was a pure ab initio method with a correction (MP2) for configuration interaction, and the second was a hybrid DFT method used with two different basis sets. The resultant structures are shown in Figure 1. The starting structures in each case were the AM1 classical ions **1** and **3** shown in Figure 2. For the bicyclo[3.2.1]octyl system both methodologies and basis sets gave very similar structures; the same cannot be said for the bicyclo[3.2.2]nonanyl system. The MP2/6-31G*//AM1 structure was quite unlike any other encountered in this work, seemingly having formed a substituted cyclopropyl cation. Other than the formation of 2-X-bicyclo[3.2.2]nonane, no other possible products from this ion have been reported. All other computations were confined to the B3LYP/6-31G* method.

The first detailed structure to be examined was that of the 2-bicyclo[3.2.1]octanyl cation since the evidence for the nonclassical structure seems well accepted in the literature. The classical starting ion **1** and the optimized structure **2** are shown in Figure 2. The nonclassical ion **2** is 11.3 kcal/mol more stable than **1**. This compares favorably with the calculated advantage of the nonclassical 2-norbornyl cation over its classical analogue (13−14 kcal/mol).[10]

The same procedure was followed in optimizing the classical version of the 2-bicyclo[3.2.2]nonanyl cation (**3**). The optimized structure is shown as **4**. As indicated, the bridging carbon-8 has moved toward the cation center over the C1−C2 bond. However as seen, ion **4** is not symmetrical. In keeping with the energies cited above, **4** is more stable than **3** by 11.5 kcal/mol. Okazaki et al.[4] reported the $^{13}$C label, initially 100% at C2 in the tosylate starting material, to be distributed between carbons 1 and 2 in an approximate 3:2 ratio in the 2-bicyclo[3.2.2]nonyl product when the reaction was carried out in trifluoroethanol. Considering only a classical Wagner−Meerwein process, they concluded that the reaction of the 2-bicyclo[3.2.2]nonyl cation with solvent was faster than its rearrangement to the mirror-image analogue. The same conclusion must hold for ion **4** to account for their $^{13}$C results. Internal return in the cation−tosylate ion pair had been reported by Goering and Sloan.[2] Reasonably some fraction of the scrambling observed was due to this process though the barrier to scrambling the label via the mirror-image of **4** is no doubt quite facile.

**Table 1. Energies (hartrees) for Classical Ions, Nonclassical Ions, and Transition Structures**[a]

| | | | relative energy[b] |
|---|---|---|---|
| Classical Ions (B3LYP/6-31G*//AM1) | | | |
| 2-bicyclo[3.2.1]octanyl (**1**) | -312.369670 | | |
| | -312.458416 | | −55.7 |
| 2-bicyclo[3.2.2]nonanyl (**3**) | −351.677917 | | |
| | −351.773040 | | −59.7 |
| 8-bicyclo[3.2.2]nonanyl (**5**) | −351.679545 | | |
| 2-bicyclo[3.3.1]nonanyl (**8**) | 351.687201 | | |
| Nonclassical Ions (B3LYP/6-31G*) | | | |
| **2** | −312.387736 | **1** → **2** | −11.3 |
| | −312.472071 | | −8.6 |
| **4** | −351.696331 | **3** → **4** | −11.6 |
| | −351.77943 | | −4.0 |
| **6** | −351.701551 | **5** → **6** | −13.8 |
| **9** | −351.702815 | **8** → **9** | −9.0 |
| Transition Structure | | | |
| **7** | −351.670324 | **5** → **7** | 6.0 |

[a] Relative energies in kilocalories per mole. The structures are given with numbers in Figure 2. The first entry is the in vacuo value. The one below is the solvent-corrected value (PCM method) with the dielectric constants of methanol (32.6) employed. [b] The effect of the solvent correction on ions **1** and **3**.

Processes involving ions always require consideration of the effects that the solvent may have on relative ion stabilities. In Gaussian 98 ab initio corrections for solvent effects are based on the Onsager reaction field model wherein the ion is placed in a cavity surrounded by a continuous dielectric. The more advanced methods of describing the cavity attempt fitting the cavity to the shape of the molecule. In this case, the polarized continuum model (PCM) of Miertius and Tomasi[11] was employed using the dielectric constant for methanol ($\epsilon = 32.6$). More sophisticated methods of cavity description were found to require prohibitive amounts of workstation time. The results for structures **1**−**4** are given in Table 1. It is reasonable to expect the solvent effect to be more pronounced for the classical ions with their more highly localized charge density than for the nonclassical ions whose charge occupies a larger volume of space. The energy change in going from classical ion **1** to nonclassical **2** decreases to 8.6 kcal/mol, while the lowering effect for **3** to **4** drops the energy difference to 4.0 kcal/mol. In both cases, however, the nonclassical ion remains the more stable of the pair. There is no reason to believe this

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(10) (a) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. *J. Org. Chem.* **1997**, *62*, 4216. (b) Schleyer, P. v. R.; Maeker, C. *Pure Appl. Chem.* **1996**, *67*, 755.

(11) Miertius, S.; Tomasi, J. *J. Phys. Chem.* **1982**, *65*, 239.

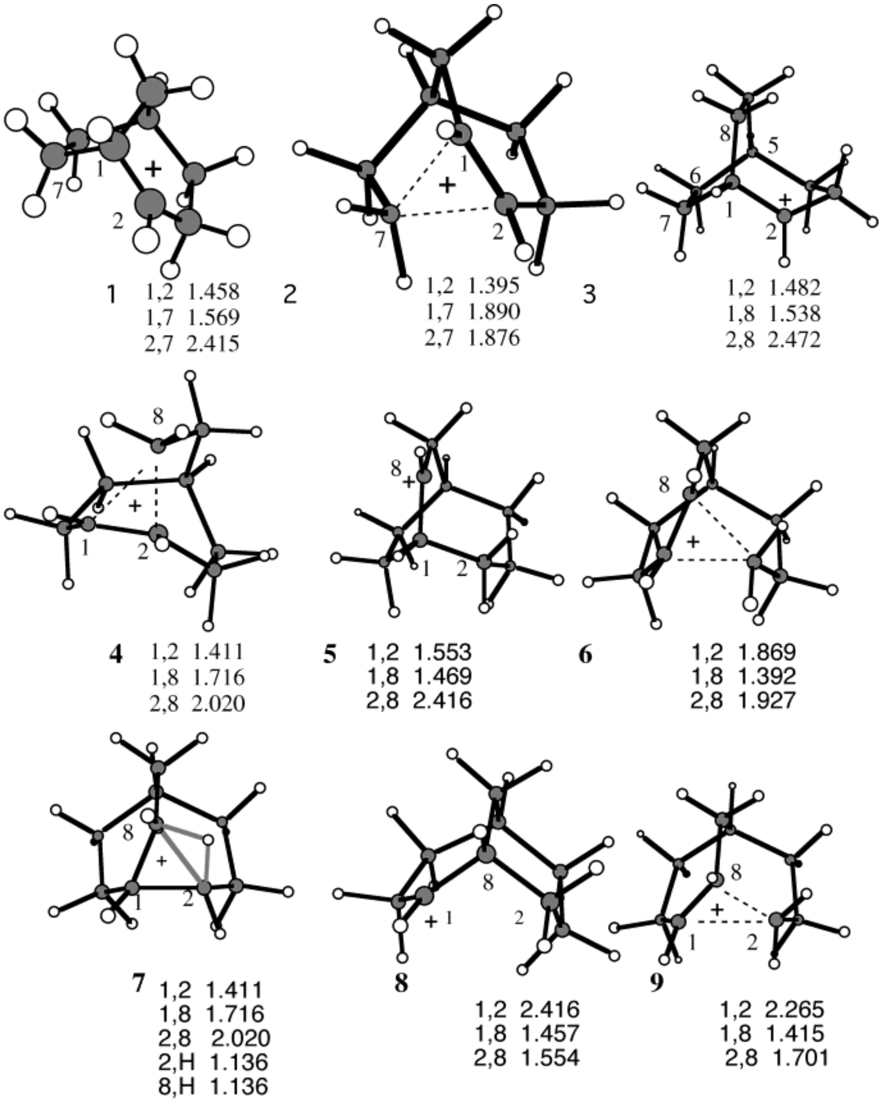
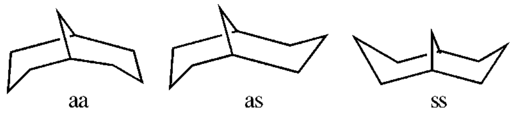


**Figure 2.** Structures and essential bond lengths (Å) of interest from this study.

situation would change with the other nonclassical carbocations in this study.

Okazaki et al.[5] reported the partial $^{13}C$ NMR chemical shifts and attached protons for their starting materials and products without giving assignments. Reference is made to the use of "authentic" samples without further details. Only two $^{13}C$ NMR spectra were produced in their supplemental data. Product proof for the compounds in this study requires adequate assignment of the carbon spectra particularly if stereochemical information is to be inferred. In their useful small volume, Whitesell and Minton[12] report the $^{13}C$ NMR spectra for a number of important bicyclic hydrocarbons as well as many substituted members of these families. Among those on the list are bicyclo[3.3.1]nonane and bicyclo[3.2.2]nonane, whose values are reproduced in Table 1. A number of substituted bicyclo[3.3.1]nonanes are included though none of these have substituents in the 2-position. The Japanese group refers to a rational preparation of 2-bicyclo[3.2.2]-nonanol by Kirmse and Feldman.[13] However, no spectral data are to be found there. A flag is raised concerning the correct identification of some portion of the solvolysis products. The question of assignments will now be considered.

### Scheme 1



An examination of the bicyclo[3.3.1]octane system indicates three conformers must be considered. These are illustrated in Scheme 1. Referencing to carbons **3** and **7**, these may be designated as *anti*−*anti*, *anti*−*syn*, and *syn*−*syn*. The *aa* conformer is 3.7 kcal/mol more stable than its *ss* counterpart (AM1) with the *as* conformer intermediate in energy. The barrier to flipping from the *aa* configuration to the *as* configuration is 2.8 kcal/mol. In an equilibrium mixture of these conformers the *aa* species will dominate the virtual exclusion of the other two. The GIAO NMR chemical shifts (BPW91/6-311G**//B3LYP/6-31G*) for the *aa* conformer of the [3.3.1] hydrocarbon and the [3.2.2] hydrocarbon were calculated and compared with the values reported[12] in Table 2. Between the experimental and calculated chemical shifts,

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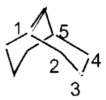
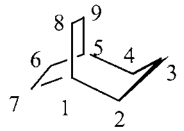
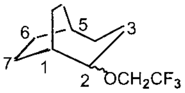
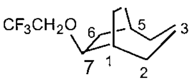
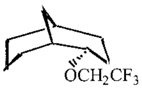
[12] Whitesell, J. K.; Minton, M. A. *Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy*; Chapman and Hall: New York, 1987.

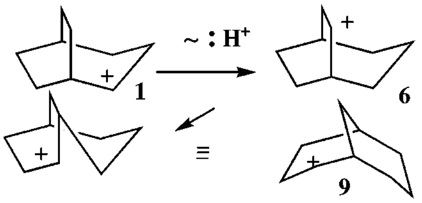
[13] Kirmse, W.; Feldmann, G. *Chem. Ber.* **1989**, *122*, 1531.

**Table 2. NMR C−13 Chemical Shift Calculations (BPW91/6-311G**/B3LYP/6-31G*)**

| |  | |  | |  | | |  |  |  | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Axial | Equit. | | | | | |
| | Exp[a] | Calc'd | Exp[a] | Calc'd | Calc'd | Calc'd | Exp[b] | Calc'd | Calc'd | Calc'd | Exp[b] |
| 1 | 29.0 | 32.3 | 28.0 | 30.7 | 37.7 | 35.8 | 33.7 | 39.6 | 35.8 | 37.7 | 31.9 |
| 2 | 35.7 | 37.1 | 31.6 | 32.4 | 78.7 | 82.4 | 87.4 | 40.1 | 82.4 | 78.7 | 81.4 |
| 3 | 22.4 | 23.0 | 22.6 | 23.9 | 29.9 | 25.6 | 23.4 | 27.0 | 25.6 | 29.3 | 26.6 |
| 4 | 35.7 | 37.1 | 31.6 | 32.4 | 34.4 | 27.4 | 24.1 | 36.2 | 27.4 | 34.4 | 27.2 |
| 5 | 29.0 | 32.3 | 28.0 | 30.7 | 33.1 | 30.0 | 27.8 | 34.3 | 30.0 | 33.1 | 27.1 |
| 6 | 25.9 | 23.5 | 31.6 | 32.4 | 35.8 | 31.9 | 29.3 | 33.9 | 31.9 | 35.8 | 31.4 |
| 7 | 25.9 | 23.5 | 22.6 | 23.9 | 26.7 | 22.0 | 19.1 | 78.1 | 22.0 | 26.7 | 20.7 |
| 8 | 25.9 | 23.5 | 31.6 | 32.4 | 29.8 | 28.8 | 27.7 | 27.5 | 28.8 | 29.8 | 28.0 |
| 9 | 25.9 | 23.5 | 35.0 | 35.1 | 38.1 | 28.1 | 26.8 | 31.2 | 28.1 | 38.6 | 27.8 |
| $CH_2$ | - | | | | 67.5 | 65.2 | | 73.0 | 65.2 | 67.5 | |
| $CF_3$ | - | | | | 145.6 | 133.7 | | 145.3 | 133.7 | 145.6 | |

[a] See ref 12. [b] See ref 5.

**Scheme 2**



the agreement is generally within 1−3.0 ppm with only a few exceptions.

The two conformers shown for the 2-bicyclo[3.2.2}-nonanyl trifluoroacetate differ only by 0.6 kcal/mol (molecular mechanics MMX force field) to 2.1 kcal/mol (semiempirical AM1). The result favored the ester group as being equatorial in each case. The reported $^{13}$C chemical shifts were compared to the calculated values. The best fit was to the calculated values for the equatorial ester (average deviation 2.5 ppm compared to 6.9 ppm).

In contrast, consideration of the equatorial and axial conformers of the 2-bicyclo[3.3.1]nonanyl trifluoroethyl ether (Table 2) shows an excellent fit between the experimental data and the calculated chemicals shifts for the axial (*exo*) ether. The assignment of the experimental data was conducted with regard to optimizing the fit. The average deviation for the *exo*-2-bicyclo[3.3.1]nonanyl trifluoroethyl ether (axial) was 1.0 ppm, while the *endo* (equatorial structure) analogue gave an average deviation of 4.6 ppm. As will been seen, this has mechanistic implications.

Okazaki et al.[4] considered the classical 1,2-shift mechanism the best explanation for their data, writing the process for achieving an intermediate in the bicyclo[3.3.1] system as shown in Scheme 2. Optimization of the 8-bicyclo[3.2.2]nonanyl cation **5**, however, shows it to be a nonclassical ion (**6**). Ion **6** is 13.8 kcal/mol more stable than its classical analogue.

In attempting to answer the question of the role played by **6**, it became clear that the process was not the two steps proposed, but rather that a concerted migration and rearrangement of **4** to the bicyclo[3.3.1] system occurs through transition structure **7** with an activation enthalpy of only 16.3 kcal/mol. Structure **7** resembles that of an edge-protonated cyclopropane.[14] The fate of **7** was examined by an intrinsic reaction coordinate (IRC) calculation.[14] A frequency calculation tests the TS, establishing validity by the presence of an imaginary vibrational frequency corresponding to the motion along the reaction coordinate. The force constants for this motion plus all others are then used to move the TS off the energy maximum in small increments. The default values in the program provide twelve data points, six moving in each direction along the reaction coordinate from the transition structure. The terminal points in this process can then be optimized in the conventional manner. For most systems the results correspond to the starting and final product(s) associated with that TS. However, the optimization will carry the starting structure to the nearest stable minimum, which may differ from the expected structures. Such is the case here. The early structure reverts to ion **6** rather than **4** since **6** is 3.3 kcal/mol more stable. In the forward direction the IRC produces ion **9** discussed below.

The final intermediate proposed by Okazaki et al.[4] was the 2-bicyclo[3.3.1]nonanyl cation **8**, which optimizes to the ion **9**, which is lower in energy than **8** by 9.8 kcal/mol. Superficially **9** has the features of a classical ion. The C1−C2 bond is materially shortened in reference to **8**, while the 2,8-bond is somewhat lengthened**.** The C1−C8−C2 angle has closed to 83° as compared to 93° for the same angle in **8**.

In **9** the charge distribution derived from the electrostatic potential[15] on C1 is 0.17e, while that on C8 is only 0.07e. In contrast, these values for ion **6** are −0.04e and 0.18e, respectively. A reviewer has questioned whether either ion **6** or **9** might be an artifact. Obviously the PES for the bicyclic $C_9H_{10}$ cation system is extremely complex with a number of shallow minima and several maxima. Both ions **6** and **9** exhibit all positive vibrational frequencies, characterizing them as stable minima. There are some differences in bond lengths in those portions

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(14) Koch, W.; Schleyer, P. v. R.; Buzek, P.; Liu, B. *Croat. Chim. Acta* **1992**, *65*, 655.

(15) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(16) Singh, U. C.; Kollman, P. A. *J. Comput. Chem.* **1984**, *5*, 129.

concerned with the bridged ion structures. The HOMO for **9** shows a strong bonding interaction between C2 and C8, with a pronounced volume forming the partial $\sigma$ bond between C1 and C8. The charge differential in **9** may account for the failure of all workers to date in identifying any products derived from attack at C8. To summarize, the reaction path proceeds from **4** to **7** to **9**. Ion **6** is not on the reaction pathway arising only through minimization of ion **5** and/or the initial point on the IRC from **7**.

No experimental data on the stereochemistry of the 2-bicyclo[3.3.1]nonanyl trifluoroethyl ether product have been published.[4] However, the calculated chemical shifts reported in Table 2 and the data on the spectrum of the reaction product mixture given by the Japanese are most consistent with the *exo*-2-trifluoroethyl ether. One can just see a quartet at the edge of the product $^{13}$C spectrum (their supplemental data) and centered at ca. 129 ppm. The data stop shortly beyond this point. The formation of 2-bicyclo[3.3.1]nonanyl trifluoroethyl ether is consistent with attack of the solvent at C1 on **9**.

## Conclusions

One of the major tools in addressing the nature of the process in carbocation solvolysis reactions has been the stereochemical results produced. The published mechanism postulated a rearrangement proceeding through a classical Whitmore multistep pathway. Only intermediate ions with the charge localized on one carbon were envisioned. However, the reaction products were described as containing only the *exo*-2-bicyclo[3.3.1]nonanyl product. No rationalization was offered for the failure to observe the formation of the corresponding *endo* product, certainly an expected product of a classical carbocation rearrangement.

DFT computations have established that none of the classical cations postulated by Okazaki et al.[4] exist in the form stated therein. Nonclassical forms dominate the mechanism by 10−15 kcal/mol of enhanced stability over their classical counterparts. The transit from the bicyclo[3.2.2] system to the bicyclo[3.3.1] system is most reasonably a concerted process via transition structure **7**. The calculated $^{13}$C NMR chemical shifts for a number of bicyclic molecules have been presented.

**Supporting Information Available:** DFT data. This material is available free of charge via the Internet at http://pubs.acs.org.

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