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Structures, Energies, and Modes of Interconversion of $C_4H_7^+$ Ions

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Abstract: The potential energy surface involving the cyclopropylcarbinyl and cyclobutyl cations is investigated with ab initio molecular orbital calculations. The relative energies of many proposed structures are given at the MP4SDTQ/6-31G*//MP2(FULL)/6-31G* level of theory and compared with experimental observations of the stable ion in solution. The puckered cyclobutyl cation (symmetrical bicyclobutonium ion) is slightly less stable than the bisected cyclopropylcarbinyl cation, but both are energy minima. Roberts' unsymmetrical bicyclobutonium ion is the apparent transition state that connects these species. The chemical shifts of the stable ion solution at various temperatures are found to be in close agreement with those calculated with the IGLO approach. The pathway of interconversion between the cyclopropylcarbinyl and bicyclobutyl ions is studied by using electron correlated optimizations away from the symmetric stationary points. The 3-fold degenerate rearrangement barrier is very low, but possible "tricyclobutonium ions" with 3-fold symmetry are not involved. Mechanisms that interchange the protons within the ionic system are discussed and compared with experimental limits. Hydrogen exchanges via a planar cyclobutyl cation and via 1,2-H shifts both appear to be possible but 1,3-H shifts require much higher activation.

The $C_4H_7^+$ ion has been the subject of a number of experimental[1-7] and theoretical investigations.[8-11] This interest stems from the observation that cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives generate, under similar conditions, similar product distributions of all of the three (approximately 10:10:1).[1b]

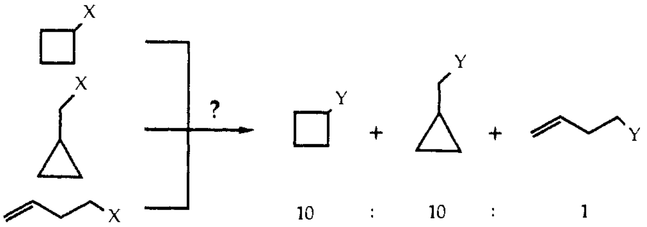

Diagram 1

The nature of the common intermediates has unfolded under both experimental and theoretical scrutiny. Early solvolysis studies of the cholesteryl–*i*-cholesteryl system led to the proposal of a homoallylic ion as the most stable isomer, in equilibrium with the cyclopropylcarbinyl ion.[2] ^{14}C tracer studies on the parent system showed extensive, but not statistically random scrambling of the ^{14}C among the methylene carbons during deamination. This was first interpreted as indicating a 3-fold symmetric, nonclassical tricyclobutonium structure as an intermediate (Diagram 2).[3a]

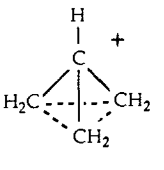

Diagram 2

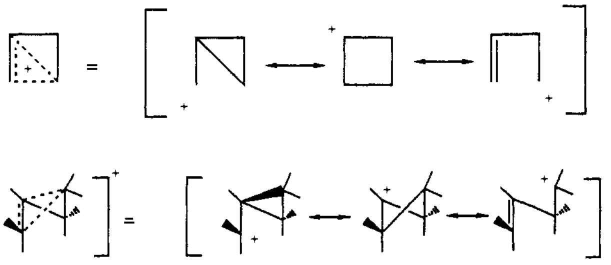

Diagram 3

Further work led to the revised hypothesis that the common intermediate was an unsymmetrical bicyclobutonium ion perhaps in equilibrium with a bisected cyclopropylcarbinyl cation.[3b] The bicyclobutonium structure was described as a resonance hybrid of cyclopropylcarbinyl, cyclobutyl, and homoallyl ions (Diagram 3). Attack of solvent at any of the three carbons formally sharing the charge would lead to one of the three reaction products. Others discounted the contribution of nonclassical ions and favored an

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(1) Experimental reviews: (a) Richey, G. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol III, Chapter 25. (b) Wiberg, K. B.; Hess, B. A.; Ashe, A. J. *Ibid.* Chapter 26. (c) Brown, H. C. (with comments by Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum: New York, 1977; Chapter 5. (d) Friedrich, E. C. In *The Chemistry of the Carbonyl Group*; Rappoport, Z., Ed.; Wiley-Interscience: New York, 1987; Chapter 11. (e) Vogel, P. *Carbocation Chemistry*; Elsevier Pub.: New York, 1985. (f) Bartlett, P. D. *Nonclassical Ions*; W. A. Benjamin, Inc.: New York, 1965.

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equilibrium between the classical cyclopropylcarbinyl cations with a small contribution of the puckered cyclobutyl cation (Diagram 4),[4] although there was some difficulty accounting for the homoallylic products given the relative stabilities expected for the classical homoallylic cations.

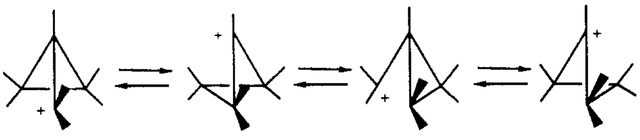


Diagram 4

Solvolysis of specifically labeled cyclopropylcarbinol derivatives demonstrated that the rearrangement process proceeded stereospecifically under solvolytic conditions.[5] This requires that the exo and endo hydrogen positions within the ion are distinct and do not readily interconvert, and that any cyclobutyl cation formed as an intermediate in the rearrangement remains puckered and does not invert. This is not the behavior expected for a classical cyclobutyl cation.

NMR studies of the stable ion solution of the parent ion showed that the three methylene carbons were equivalent on the NMR time scale.[6a,b] This implies that the ion either had 3-fold symmetry or was a rapidly equilibrating set of ions of lower symmetry. A slight temperature dependence of the ^{13}C chemical shifts suggested a rapid equilibrium between two or more chemically distinct isomers. From the line widths, an upper limit of 2.0 kcal/mol was estimated for the barrier to rearrangement.[6c] Isotopic perturbation of the parent ion by deuterium on one methylene produced a relatively large, temperature-dependent splitting in the averaged methylene signal.[7] This confirmed the proposal of rapid equilibration of isomers of lower than 3-fold symmetry. The CMR spectrum of ion made from monodeuteriated precursor was particularly striking. Two isotopically perturbed multiplets were observed indicating two isotope effects opposite in sign and magnitude from one another. This was interpreted as indicating that the exo and endo C–H bonds on one methylene carbon have significantly stiffer and less stiff than normal bonding force constants. The only proposed structure that contained a carbon center likely to lead to such a difference in bonding was the bicyclobutonium ion, possessing a pentacoordinated carbon. A specifically endo labeled ion demonstrated that the exo C–H(D) isotope effect led to a down-field shift while the endo C–H(D) effect lead to an upfield shift of lesser magnitude.[7b,c] This lead to the prediction that the exo C–H bond was significantly stiffer than the endo.

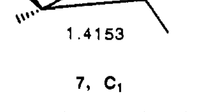
Theoretical Background

Early theoretical studies have had limited success explaining the observed properties of the ion.[8] Semiempirical calculations with the MINDO/3 technique found a puckered cyclobutyl ion (symmetrical bicyclobutonium ion) to be the lowest energy structure,[9] but the calculated barrier to interconversion through the bisected cyclopropylcarbinyl structure was too great in comparison with the experimental upper limit. Early ab initio molecular orbital calculations reported the bisected cyclopropylcarbinyl structure to be the lowest minimum on the $C_4H_7^+$ potential surface.[10] The puckered cyclobutyl structure was found to be a saddle point by vibrational analysis of the optimized geometries at the 4-31G level of theory. Homoallylic structures collapsed without barrier to the bisected cyclopropylcarbinyl cation. The observed NMR results were explained as being due to a rapid equilibrium between the cyclopropylcarbinyl structure and a structure (C_1 symmetry) of slightly higher energy (1.5 kcal/mol at 4-31G//4-31G and 0.5 kcal/mol at 6-31G*//4-31G).[10b] The C_1 ion differed from the symmetric structure by a twist of the carbinyl carbon. Although the authors considered this structure to be similar to a bicyclobutonium ion, the exo and endo C–H bonds were not different enough to account for the isotopic perturbation results. More recently, it was demonstrated that the inclusion of electron correlation resulted in a reordering of the relative energies.[10d] Geometry optimization with MP2-(FULL)/6-31G* followed by single-point calculations at MP4SDQ/6-31G*//MP2(FULL)/6-31G* found the bicyclobutonium structure to have a lower energy than the bisected cyclopropylcarbinyl cation by 0.7 kcal/mol.

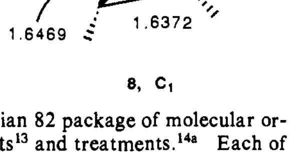
It is the purpose of the present investigation to extend and to augment the study of this complex potential energy surface. The structures and energies of a large number of isomers are determined by using rather large, flexible basis sets descriptions. The inclusion of electron correlation and its effect upon the energies and structures within the system are studied. Pathways of carbon scrambling are investigated by using electron correlated optimizations. A number of proton interchange mechanisms are addressed and compared with experimental observations. The ^{13}C chemical shifts are determined with the IGLO treatment and compared with experimental measurements of the stable ion solution. Each stationary point is characterized by vibrational analysis in order to determine its eigen-space character (i.e., whether the point is a minimum or transition state) and its zero-point energy for correction of relative energy comparisons. The force constants of the most stable isomers are examined and compared with that expected given the experimental observations.

Calculations

The structures considered were the C_s bisected cyclopropylcarbinyl cation (**1**), the twisted structure of the earlier study[10b] (**2**), a slightly puckered, C_s cyclobutyl cation with an equatorial methine C-H (**3**), a much more puckered C_s cyclobutyl structure with axial hydrogen (**4**), herein named the bicyclobutonium ion to distinguish it from **3**, the C_s planar homoallyl cation (**5**), and a 3-fold symmetric tricyclobutonium ion (**6**), which has a triplet ground state. In the diagrams in Chart I, the values outside of the parentheses are the MP2(FULL)/6-31G* optimized distances, while the values in parentheses are the HF/6-31G* optimized distances. Hydrogen rearrangement and exchange pathways were investigated by studying the planar cyclobutyl cation,**9** (C_{2v}), the perpendicular cyclopropylcarbinyl cation, **10**(C_s), the 1,2-H shift transition state, **11** (C_s), the 1,3-H shift transition state, **12** (C_{2v}), and the perpendicular homoallyl cation, **13** (C_s). Another C_{3v} structure, in which the C–H bonds of the methylene carbons are perpendicular to the methine–methylene bonds, **14**, also was considered. In addition, the pathways of carbon rearrangement were studied by optimizations away from **1** and **4** on electron correlated surfaces to structures **7** and **8** (see later text for discussion).



7, C_1



8, C_1

All calculations employed the Gaussian 82 package of molecular orbital programs[12] with standard basis sets[13] and treatments.[14a] Each of

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(10) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5917. (b) Levi, B. A.; Blurock, L. S.; Hehre, W. J. *J. Am. Chem. Soc.* **1979** *101*, 5537. (c) Cremer, D.; Kraka, E.; Lee, T. S.; Bader, R. F. W. *Ibid.* **1983**, *193*, 5069. (d) McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908. (e) Rauk, A., private communication.

(11) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* previous paper in this issue. These authors have found another structure which corresponds to the C_1 structure of ref 10b which has no imaginary frequencies at HF/6-31G* and one imaginary frequency at MP2/6-31G**. This apparent transition state in the methylene rearrangement pathway is quite different than **2** (NIMAG = 1 at HF/6-31G*) reported here. This is most likely a consequence of slightly differing starting geometries and the extremely flat nature of the potential energy surface, leading to starting structures on different "sides" of the inflection point of the surface. The minimization algorithms would then optimize each toward the nearest stationary point (their's away from the symmetric **1** and ours towards it).

(12) Gaussian 82, CRAY version K: Binkley, J. S.; Frisch, M. J.; Defrees, D. J.; Raghavachari, K.; Whitesides, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Department of Chemistry, Carnegie Mellon University, Pittsburgh PA; modified by Convex for the C1 computer in Erlganen.

Chart I

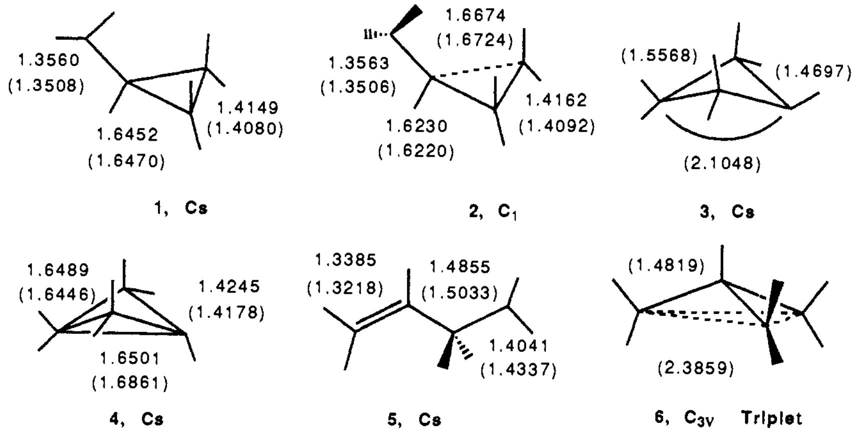

Chart II

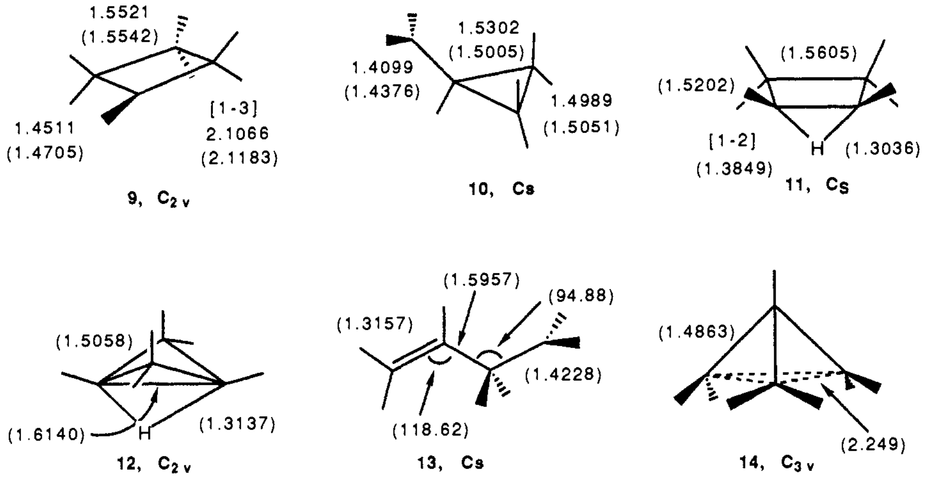

Table I. Totals Energies of the $C_4H_7^+$ Ions[a,f]

	A[b]	B	C	D	E	F	G	ZPE[c]
1	−155.227 78 (1)	−155.724 82	−155.757 49	−155.784 56	−155.744 71	−155.758 30	−155.785 89	65.41
2	−155.227 78 (1)	−155.724 78	−155.757 46		−155.744 69	−155.758 27		65.42
3[d]	−155.208 33 (0)	−155.693 86	−155.732 42					64.41
4	−155.223 81 (1)	−155.727 26	−155.759 37	−155.785 14	−155.747 66	−155.760 30	−155.786 47	66.12
5	−155.189 88 (2)	−155.671 27	−155.710 18	−155.733 18	−155.693 04	−155.712 20	−155.739 90	62.60
6	−155.116 33 (1)	−155.585 93	−155.626 09	−155.650 46				64.12
7					−155.744 70	−155.758 29		
8					−155.747 66	−155.760 29		
9	−155.208 18 (1)	−155.693 27	−155.732 02	−155.756 58	−155.713 60	−155.732 90	−155.757 93	64.09
10	−155.178 87 (1)	−155.664 53	−155.700 92	−155.726 50	−155.684 29	−155.701 44		63.93
11	−155.196 51 (1)	−155.693 65	−155.729 60	−155.754 41				64.67
12	−155.157 78 (1)	−155.666 14	−155.698 30	−155.724 68				64.18
13	−155.185 88 (1)	−155.669 57	−155.706 98	−155.733 93				64.03
14	−155.069 57 (2)	−155.580 52	−155.611 35	−155.643 58				64.39
	A[e]	B[e]	C[e]					
4	−155.234 91	−155.781 67	−155.816 45					
11	−155.210 68	−155.749 01	−155.787 88					
12	−155.173 25	−155.723 74	−155.758 59					

[a] The absolute energies are expressed in atomic units. [b] The number of imaginary frequencies is given in parentheses. See Table III. [c] The zero-point energies are in kcal/mol calculated by using the HF/6-31G* approximation. [d] Structure 3 collapses to 4 upon MP2/6-31G* optimization. See text. [e] The 6-31G** basis set, augmented by polarization functions on hydrogens, was employed for an improved description of the H-bridging structures. The 6-31G* geometries were used. [f] A = HF/6-31G*//HF/6-31G*, B = MP2(FC)/6-31G*//HF/6-31G*, C = MP3(FC)/6-31G*//HF/6-31G*, D = MP4SDTQ/6-31G*//HF/6-31G*, E = MP2(FULL)/6-31G*//MP2(FULL)/6-31G*, F = MP3(FC)/6-31G*//MP2(FULL)/6-31G*, G = MP4SDTQ/6-31G*//MP2(FULL)/6-31G*.

the structures, **1**–**6** and **9**–**13**, was first optimized with the HF/6-31G* level of approximation. The only constraint imposed upon the structures was to maintain the indicated symmetry. A vibrational analysis was performed upon each at the same level of theory in order to determine

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(13) 6-31G* and 6-31G**: Hariharan, R. C.; Pople, J. A. *Theor. Chim. Acta.* **1973**, *28*, 213. See ref 14a.

(14) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

whether they were intermediates or transition states. Single-point calculations were then carried out with full fourth-order Møller–Plesset perturbation theory[14] (MP4SDTQ) with the frozen-core approximation. Structures **1**–**6**, **9**, and **10** were further optimized by using the MP2-(FULL)/6-31G* level of theory and then subjected to full fourth-order MP(FC)4HF and UMP theory was used for the triplet, **6**. See Table I for the absolute energies and Tables II for the relative energies of the structures considered.

Relative Energies and Geometries

At the HF/6-31G* level of approximation, **1**(C_s, *N*umber of *IMAG*inary frequencies = 1) and **2** (C_1, NIMAG = 1)[11] are energetically indistinguishable (**1** is 0.001 kcal/mol higher in energy than **2**) although the two geometries are distinctly different. In the cyclopropyl ring of **1**, the methine–methylene distance is 1.647 Å while the two corresponding distances in **2** are 1.622 and 1.672 Å. The methylene–methylene distances in **1** and **2** are 1.408 and 1.409 Å, respectively. The methine–carbinyl distances for **1** and **2** are both 1.351 Å. These structures are only a small distortion from each other. In fact, if one looks at the imaginary vibrational mode for **1**, the unit displacement vectors would move the atoms of **1** in the directions necessary to reach **2** (Diagram 5). In the following discussion of the Hartree–Fock results the energies will be given relative to that for **2**.

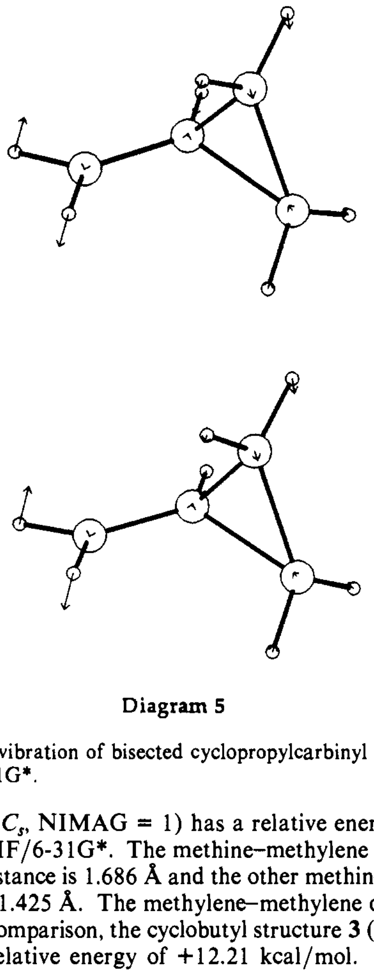

Diagram 5

imaginary vibration of bisected cyclopropylcarbinyl cation at HF/6-31G*.

The ion **4** (C_s, NIMAG = 1) has a relative energy of +2.50 kcal/mol at HF/6-31G*. The methine–methylene bridgehead-bridgehead distance is 1.686 Å and the other methine–methylene distances are 1.425 Å. The methylene–methylene distances are 1.649 Å. In comparison, the cyclobutyl structure **3** (C_s, NIMAG = 0) has a relative energy of +12.21 kcal/mol. The bridgehead–bridgehead distance is 2.105 Å, the methine–methylene distance is 1.470 Å, and the methylene–methylene distance is 1.557 Å.

The planar homoallyl structure **5** had a relative energy of +23.78 kcal/mol. The methylene–methine C–C distance of the formal double bond is 1.322 Å. This is analogous to the methine–carbinyl distance in **1** and **2**. The other methylene–methine distance is 1.504 Å and the methylene–methylene distance is 1.434 Å. Structure **13** had a relative energy of +26.29 kcal/mol. The methylene–methine distance of the formal double bond is 1.315 Å and the other methylene–methine distance is a short 1.427 Å.

The ion **6** has a triplet ground state in C_{3v} symmetry, 69.93 kcal/mol (UHF/6-31G*) less stable than **2**. The methine–methylene distance is 1.423 Å and the distance between each methylene is a rather distant 2.386 Å. Similarly, **14** has a relative energy of 99.28 kcal/mol. The methine–methylene distances are 1.486 Å with the distance between methylene carbons being 2.249 Å.

The structures **9**–**14** were examined in order to determine the plausibility of their participation in the hydrogen exchange processes. The planar cyclobutyl cation **9** (C_{2v}, NIMAG = 1) is calculated to be 12.30 kcal/mol less stable than the most stable structures. The methine–methylene distances are 1.470 Å and the methylene–methylene distances are 1.554 Å. The perpendicular cyclopropylcarbinyl structure **10** is 30.69 kcal/mol above **1** and **2**. In comparison to **1**, the cyclopropylcarbinyl methine–methylene distances are shorter, at 1.500 Å, and the methylene–methylene distance is longer, being 1.505 Å. The methine–carbinyl distance is much longer at 1.438 Å than in **1**.

Structures **11** and **12** represent the transition states for 1,2- and 1,3-hydrogen transfers, respectively, between carbon centers. The C_s 1,2-H shift structure, **11**, has a planar cyclobutyl ring with the transferring hydrogen equidistant between two carbons. The hydrogen is 1.104 Å away from the midpoint of the C–C bond and 1.304 Å away from either carbon. The carbon–carbon bond involved in the hydrogen transfer has shortened to 1.385 Å from the 1.470 Å of **9**, the two symmetrically equivalent bonds are 1.520 Å, and the bond opposite to the transferring hydrogen is 1.600 Å. This structure is 19.62 kcal/mol less stable than **2**. The C_{2v} 1,3-hydrogen shift transition state, **12**, is 43.93 kcal/mol less stable than the minimum energy structures. The bridgehead–bridgehead distance has lengthened to 1.614 Å and the bridgehead–methylene distances are 1.506 Å.

Inclusion of electron correlation by single-point calculations on all of the HF/6-31G* optimized geometries using full fourth-order Møller–Plesset perturbation led to a significant reordering of the relative energies. At all correlated levels the bicyclobutonium structure **4** becomes the most stable structure. However, after correction for the zero-point energies, **1** becomes more stable than **4** by 0.26 kcal/mol (also with the MP2-(FULL)/6-31G* geometries). At the MP4SDTQ/6-31G*//HF/6-31G* + ZPE level, classical ions like **5**, **9**, **10**, and **13** increase in relative energy, and triplet **6** especially so. The H-bridged species **11** and **12**, as well as **14**, are favored. Such effects have been observed in other cationic systems, in which delocalized structures are found to be stabilized to a much greater extent by electron correlation than localized isomers.[15]

As electron correlation was crucial in the relative ordering of the energies of the isomers, optimization were carried out at MP2(FULL)/6-31G*. The orderings of relative energies did not change at either MP2(FC)/6-31G*//MP2(FULL)/6-31G*, MP2(FULL)/6-31G*//MP2(FULL)/6-31G*, MP3(FC)/6-31G*//MP2(FULL)/6-31G*, or MP4SDTQ(FC)/6-31G*//MP2(FULL)/6-31G*. Again the bicyclobutonium ion was the most stable isomer. The following relative energies are MP4SDTQ(FC)/6-31G*//MP2(FULL)/6-31G* without zero-point energy correction. The cyclobutyl structure **3** collapsed without apparent barrier to give **4**. This discounts the existence of a cyclobutyl structure between **4** and **9** as a minimum on the potential energy surface. The bicyclobutonium ion **4** puckered even further and the bridgehead–bridgehead distance decreased to 1.650 Å. This appears to be an attempt to stabilize the cationic

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(15) Bridged, or *nonclassical* structures have been shown to be lowered in energy preferentially over *classical* ions upon inclusion of electron correlation. One might expect that correlated electron distributions would be quite important in properly depicting such electron deficient species. (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 379ff. (b) Raghavachari, K.; Whitesides, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (c) Köhler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479.

(16) (a) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020. (b) Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. (c) Bremer, M.; Schleyer, P. v. R.; Schütz, K.; Kausch, M.; Schindler, M. *Angew. Chem.* **1987**, *99*, 795; *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 761.

Table II. Relative Energies of the $C_4H_7^+$ Ions[a,e]

	A	B	C	D	E	F	G	H	I	J	ZPE[b]
1	0.001	1.53	1.18	0.36	–0.26	1.85	1.26	0.36	0.63	–0.26	58.22
2	0.00	1.53	1.18								58.22
3	12.21	21.06	16.89								57.32
4	2.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	58.84
5	23.78	35.13	30.87	32.60	29.48	34.27	30.18	29.22	27.05	26.09	55.72
6	69.93	88.68	83.63	84.51	82.09						56.42
7[d]						1.86	1.26		0.64		
8						0.003	0.004		0.004		
9	12.30	21.33	17.16	17.92	16.12	21.38	17.19	17.91	15.39	16.11	57.04
10	30.69	39.36	36.68	36.80	34.86	39.77	36.93		35.03		56.90
11	19.62	21.09	18.68	19.28	18.00						57.56
12	43.93	38.85	38.32	37.93	36.21						57.12
13	26.29	36.20	32.87	32.13	30.28						56.99
14	99.28	90.65	91.69	88.83	87.30						57.31
	A[c]	B[c]	C[c]	D[c]							
4	0.00	0.00	0.00	0.00							
11	15.20	20.49	17.93	16.64							
12	38.69	36.35	36.31	36.96							

[a] Relative energies are expressed in kcal/mol. [b] Zero-point energies are expressed in kcal/mol, scaled by 0.89. [c] Used 6-31G** to place polarization functions on hydrogens so as to better describe the H-bridging structures. [d] Relative energy of **7** with respect to **1** is 0.004 kcal/mol. [e] A = HF/6-31G*//HF/6-31G*, B = MP2(FC)/6-31G*//HF/6-31G*, C = MP3(FC)/6-31G*//HF/6-31G*, D = MP4SDTQ/6-31G*//HF/6-31G*, E = MP4SDTQ/6-31G*//HF/6-31G* corrected for scaled zero-point energies at HF/6-31G*, F = MP2(FULL)/6-31G*//MP2(FULL)/6-31G*, G = MP3(FC)/6-31G*//MP2(FULL)/6-31G*, H = MP4SDTQ/6-31G*//MP2(FULL)/6-31G*, I = MP3(FC)/6-31G*//MP2(FULL)/6-31G* corrected for scaled zero-point energies at HF/6-31G*, J = MP4SDTQ/6-31G*//MP2(FULL)/6-31G* corrected for scaled zero-point energies at HF/6-31G*.

charge even further by the 1,3 interaction with the opposing methylene carbon. The remaining carbon–carbon distances did not change significantly. The optimized structure of the cyclopropylcarbinyl ion **1** was calculated to be 0.36 kcal/mol less stable than **4**. The ion **2** collapsed without barrier to **1**, substantiating the supposition that **2** was merely a small geometric distortion of **1** on the HF/6-31G* potential energy surface.

Structures **9** and **10** were also optimized with MP2(FULL)/6-31G* and at MP3(FC) **10** was found to be 36.93 kcal/mol less stable than **4** and 35.68 kcal/mol less stable than **1**. The methine–methylene bond distances shortened slightly to 1.499 Å, the methylene–methylene distance lengthened substantially to 1.530 Å, and the methine–carbinyl distance shortened to 1.410 Å. The ion **9** rose in relative energy to 17.91 kcal/mol at MP4(FC). The methine–methylene distance shortened to 1.451 Å while the methylene–methylene distance changed little becoming 1.552 Å.

Single points at MP4SDTQ/6-311G**//MP2(FULL)/6-31G** carried out by Koch, Liu, and De Frees[11] found **4** to be more stable than **1** by about 0.5 kcal/mol. After correction for the zero-point energies at MP2/6-31G**, the two structures became equally stable.

Vibrational Analysis

Vibrational analysis of **1–6**, **9–12** at HF/6-31G* gave quite interesting results. The full zero-point energies and the scaled zero-point energies and relative energy comparisons are found in Tables I and II, respectively. The normal coordinate vibrational frequencies are found in Table III. Foremost, structures **1**, **2**, **4**, **5**, **9**, **10**, **11**, **12**, and **13** were all found to have at least one negative eigenvalue (imaginary frequency) and **5** and **14** had two.[11] This means that none of these structures are minima on the HF/6-31G* potential energy surface. Only **3** and **6** were found to be minima at this level of theory. As electron correlation is required to describe the relative energies of the extensively delocalized cations, the potential energy surface at the Hartree–Fock level is incorrect not only for the relative energies but also for the character (i.e., number of imaginary frequencies) of the stationary points. However, the normal modes, although not correct in terms of the absolute value of their associated eigenvalues, should describe the vibrational displacements of the atoms in a reasonable manner. Advantage will be taken of this later in the text.

The isotopic perturbation results are one of the more interesting facets of this cationic system.[7] The observation of two different isotope effects of different magnitude and opposite sign strongly suggests that the ion have a methylene group in which the two C–H bonds have very different force constants.[7a] Moreover, the stereospecifically labeled ion in solution demonstrated that the exo C–H bond must be a stiffer bond than the endo C–H bond.[7c] Vibrational analyses should be able to differentiate between the most likely structures using this criterion. Inspection of the internal force constants reveals that in **4** the exo C–H bond to the pentacoordinated carbon center has a force constant of 6.40 mdyn/Å while the endo force constant is 6.20 mdyn/Å. This is in comparison to the other two methylene carbons whose C–H force constants are 6.37 and 6.29 mdyn/Å, exo and endo, respectively. Thus the two force constants of pentacoordinated carbon are calculated to be quite different, as predicted from the experimental observations. The internal force constants of **1** also were examined. The exo and endo C–H force constants for both the carbinyl and the cyclopropyl–methylenes are very nearly the same. Thus the force constants of the HF/6-31G* vibrational analysis support the prediction that the bicyclobutonium ion is the major isomer in the stable ion solution.

Vibrational analyses at MP2/6-31G** (carried out by Koch et al.[11]) found both **4** and **1** to be minima on the correlated potential energy surface. The lowest frequency vibrational modes were 136 cm^{-1} for **4** and 83 cm^{-1} for **1**, indicating that the potential surface is quite flat in the neighborhood of the minima.

Calculation of the Chemical Shifts

The ^{13}C chemical shift of the isomers is another physical observable of the system that may be reproduced theoretically. Schindler has applied the IGLO (Individual Gauge for Localized Orbitals) method to the calculation of the ^{13}C chemical shifts of the $C_4H_7^+$ ion (Diagram 6).[16]

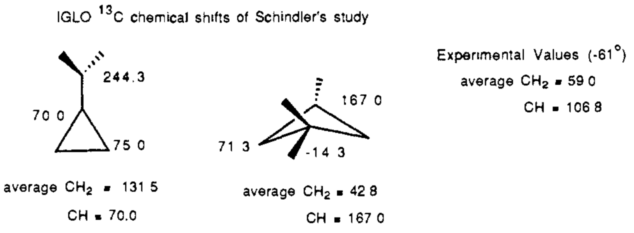
IGLO ^{13}C chemical shifts of Schindler's study

Diagram 6

The IGLO results for **4** gave a much better fit to the observed spectrum than for **1** (see Table IV). But the chemical shifts are such that one can only discount the participation of **1** as the major isomer in the rapid equilibrium. However, IGLO results are

Table III. Vibrational Analyses HF/6-31G* (Wavenumbers reported in cm^{-1})

		Bisected Cyclopropylcarbinyl Cation **1**				
−62.0	407.1	408.5	626.6	708.2	873.6	1003.6
1079.7	1141.2	1189.1	1216.9	1256.1	1279.8	1340.1
1346.6	1424.9	1543.2	1613.9	1689.9	1738.9	3353.5
3354.2	3359.5	3424.6	3453.1	3456.3	3468.5	
		Unsymmetric Cyclopropylcarbinyl Cation **2**				
−29.3	406.9	416.1	616.8	724.3	871.2	1001.8
1076.9	1146.0	1187.8	1217.6	1257.7	1280.2	1337.7
1344.7	1424.9	1544.2	1615.1	1689.8	1740.2	3350.2
3351.6	3362.8	3425.2	3449.5	3452.7	3468.8	
		Puckered Cyclobutyl Cation **3**				
108.0	472.2	583.9	808.9	934.2	940.1	972.4
984.87	1006.1	1106.1	1231.5	1309.2	1347.3	1371.4
1377.9	1434.2	1475.9	1501.8	1515.8	1642.9	3164.9
3175.3	3267.7	3268.2	3300.3	3367.1	3380.7	
		Bicyclobutyl Cation **4**				
−131.2	430.6	559.2	825.45	955.3	980.2	1010.9
1074.1	1156.3	1204.4	1238.4	1262.9	1280.0	1295.8
1355.3	1358.7	1570.4	1577.0	1675.3	1678.0	3328.7
3348.3	3351.8	3385.4	3443.6	3446.9	3455.3	
		Planar Homoallyl Cation **5**				
−377.0	−140.4	307.7	525.7	532.3	771.7	897.0
1057.7	1078.5	1123.9	1158.1	1182.9	1283.7	1401.7
1408.2	1440.8	1471.0	1581.9	1609.1	1853.9	3055.9
3056.2	3316.9	3362.2	3372.3	3460.0	3479.9	
		Tricyclobutonium Cation **6**				
393.2	408.4	408.4	445.6	723.7	723.7	945.9
951.8	951.8	964.3	1000.0	1000.0	1203.2	1203.2
1317.4	1485.7	1485.7	1623.9	1639.4	1639.4	3315.4
3354.6	3360.2	3360.2	3476.0	3476.0	3476.0	
		Planar Cyclobutyl Cation **9**				
−86.1	391.6	646.1	813.1	899.8	933.9	962.7
1002.9	1007.4	1101.2	1228.6	1310.9	1355.4	1378.2
1384.3	1433.7	1465.1	1497.3	1499.2	1639.4	3184.9
3193.7	3227.7	3229.3	3300.5	3362.7	3382.7	
		Perpendicular Cyclopropylcarbinyl Cation **10**				
−684.6	292.7	352.6	782.8	813.1	838.5	957.5
997.4	1097.6	1134.8	1204.6	1215.6	1259.8	1287.5
1307.2	1371.8	1507.9	1614.5	1640.6	1661.9	3159.1
3311.5	3327.8	3335.0	3422.4	3426.5	3434.3	
		1,2-H Shift **11**				
−258.6	346.4	763.8	921.6	952.0	960.1	987.8
1030.2	1103.3	1175.0	1273.0	1278.1	1334.2	1356.9
1379.6	1406.3	1469.9	1595.1	1598.8	1628.7	2287.1
3275.5	3279.4	3339.9	3348.0	3391.5	3409.8	
		1,3-H Shift **12**				
−824.2	585.5	875.1	892.6	909.7	965.5	1017.6
1033.7	1149.0	1175.4	1189.1	1250.6	1301.0	1315.0
1333.7	1372.2	1461.8	1636.8	1640.2	1675.5	2212.4
3331.3	3331.6	3358.1	3371.6	3424.3	3427.6	
		Perpendicular Homoallyl Cation **13**				
−219.0	163.3	394.9	446.8	628.5	747.1	901.4
1058.0	1064.4	1128.3	1167.2	1225.7	1329.4	1378.2
1390.5	1479.9	1565.2	1610.4	1686.4	1824.6	3282.5
3333.2	3349.6	3363.7	3365.3	3449.6	3452.8	
		Robert's Tricyclobutonium Cation **14**				
−429.9	−429.9	518.2	856.8	856.8	887.2	984.3
984.3	1113.2	1113.2	1130.0	1130.0	1202.2	1202.2
1324.5	1400.1	1400.1	1684.3	1684.3	1736.2	3317.0
3372.9	3372.9	3402.6	3472.7	3494.9	3494.9	

IGLO ^{13}C chemical shifts using the geometries of this study

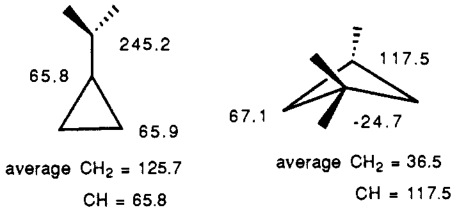

Diagram 7

sensitive to the geometry, and the structures Schindler employed in his paper were not high level. By using the MP2(FULL)/6-31G* optimized geometries of this study, the results of the IGLO treatment are improved (Diagram 7), particularly with regard to the ^{13}C chemical shifts of the CH groups. These new values calculated by using the MP2/6-31G* optimized geometries (with the chemical shifts calculated using a triple-ζ basis set with polarization on C and H) for **1** and **4** are compared with experimental data at −61° and −132° in Table IV. In agreement with other methods of analysis of these data, the fit for **4** is much better than that for **1**. However, the experimental evidence suggests at least two isomers are present in rapid equilibrium.[7a] This is consistent with the small energy difference between **4** and **1** calculated earlier[10d] and in the present work. One can, using the IGLO chemical shifts, roughly determine the relative energies between **1** and **4** in solution by calculating the mole fractions required to fit the observed average shift.[17] One then can use a simple Boltzmann relationship to predict the energy difference between the two equilibrating isomers. The predicted relative energies are shown in Table IV, along with the calculated mole fractions over a range of temperatures. At all temperatures used to measure the chemical shifts experimentally[7a] this approach predicts a predominance of **4** with a minor contribution from **1**. Over the range of temperature from −61 to −132 °C, **4** is predicted to be about 0.5 kcal/mol more stable than **1**. These values, while being subject to error in the temperature measurement, the error in measurement of the chemical shifts, and the error in the calculated IGLO chemical shifts, are in reasonable agreement with the conclusions drawn from the temperature dependance studies.[7a]

Methylene–Carbon Interchange

The theoretical investigation of the interchange of carbons within the $C_4H_7^+$ ion is an especially difficult problem in that the experimental barrier has an upper limit of 2 kcal/mol.[6c] This implies that the potential surface in the vicinity of the stationary points is extremely flat, making the determination of a distinct mechanism challenging. The pathway must also interchange the carbons with retention of configuration, e.g., the exo and endo C–H positions must not be interchanged during the interchange of carbons. The only energetically viable isomers are **4** and **1**. Both **6** and **14** are eliminated by the excessively high energies of the 3-fold symmetric structures. Structure **6** has a triplet ground state, energetically inaccessible from the other singlet ions. Furthermore, the C_{3v} singlet corresponding to **6** has a degenerate ground state that necessitates Jahn–Teller distortion to lower symmetry.[8e] In order to examine the pathway between **4** and **1**, MP2(FULL)/6-31G* optimization was performed away from the symmetric stationary points along the imaginary vibrational modes

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[17] The relative energies are determined as follows. Given a rapidly exchanging equilibrium between **1** and **4**, the observed chemical shift is a weighted average of the static chemical shifts of the interchanging positions, δ_1 and δ_4.

$$\mathbf{1} \rightleftharpoons \mathbf{4}$$

$$\delta_{exp} = \chi_1\delta_1 + \chi_4\delta_4$$

As the sum of the mole fractions is unity, one can determine the mole fraction of one isomer in terms of the observed average shift and the static IGLO values.

$$\chi_1 + \chi_4 = 1$$

$$\chi_1 = \frac{\delta_{exp} - \delta_4}{\delta_1 - \delta_4}$$

Once the relative populations of the two isomers is known, a simple Boltzmann relationship may be used to determine the energy difference between the two equilibrating participants.

$$\Delta E = -kT \ln (\chi_1)$$

Table IV. Comparison of Experimental and IGLO Chemical Shifts.

	CH_2[a]	CH_2[b]	CH_2[c]	CH	
IGLO chemical shifts					
1	65.9	245.2	125.7	65.8	
4	67.1	-24.7	36.5	117.5	
T (°C)	-61	-80	-106	-115	-132
CH_2 (ppm)[d]	58.95	56.55	53.97	52.63	50.89
CH (ppm)[d]	106.78	108.02	109.38	110.25	111.32
1[e] (%)	25.17	22.48	19.59	18.08	16.26
4[e] (%)	74.83	77.52	80.41	81.92	83.74
CH (ppm)[f]	104.5	105.8	107.4	108.2	109.1
ΔE[g]	581	573	558	537	510

[a] Symmetrically related methylenes. [b] Unique methylene. [c] Average of two methylene values. [d] Experimental values taken from ref 6d. [e] Mole fractions determined theoretically (see ref 17 for details). [f] Theoretically calculated value of CH given populations above for comparison with experimentally observed signal. [g] Relative energy of minor isomer, **1**, in cal/mol as determined from theoretical populations above.

of the HF/6-31G* vibrational analysis. Each structure was displaced along the Cartesian unit vectors corresponding to the normal mode. The unit displacement vectors were scaled to 0.1 Å. The optimization was carried out until the convergence criterion of the treatment were met. While this does not rigorously correspond to a valid normal mode on the correlated potential energy surface, it was felt that this would initially lead away from the stationary points in a reasonable fashion.

1 optimized to a stationary point **7**, which was only 0.004 kcal/mol above **1** at MP3(FC)/6-31G*//MP2(FULL)/6-31G*. Despite this small energetic change, the geometries of the two isomers were distinct. One of the methylenes of the three-membered ring twisted slightly causing the methylene–methine distance to increase to 1.657 Å. The hydrogens on the methylene twisted toward the carbinyl carbon. The other methylene–methine distance shortened to 1.633 Å. The other bond distances did not change significantly. The relatively small energetic consequences of the geometric changes implies tht the potential surface is quite flat in the region of **1**. Following a path that would correspond to the softest mode away from **1** led to a point higher in energy and this supports the supposition that **1** is a minimum on the MP2(FULL)/6-31G* potential surface.

In a similar manner, **4** optimized to a stationary point **8**, slightly higher (+0.004 kcal/mol at MP3(FC)/6-31G*//MP2-(FULL)/6-31G*) in energy but geometrically distinct. One of the methylene–pentacoordinated distances increased to 1.662 Å while the other shortened to 1.637 Å. The methylene–methine distances followed suit, but in an opposite manner. The methylene–methine distance opposite to the shortened methylene–pentacoordinated distance lengthened to 1.427 Å while the other shortened to 1.422 Å, opposite to the lengthening distance. The methylene center that moved away from the pentacoordinated center twisted such that the hydrogens moved closer to the pentacoordinated center.

The structures **8** and **7** correspond to a pathway of interconversion between **4** and **1** (Diagram 8). The rearrangement begins at **4** as one of the methylene carbons begins to twist and swing away from the pentacoordinated center to **8**. The motion continues, swinging the methylene up toward a bisected configuration. The motion continues through **7** when the once pentacoordinated center begins twisting its hydrogens into the symmetrical **1**. The nonconcerted nature of the methylene twist from **7**–**1** implies that **7** may not be directly on the pathway of interconversion.[18] Nevertheless, this pathway can be considered a good description of the mechanism of carbon interchange. The mechanism has a barrier of less than 2 kcal/mol involves the rapid equilibrium of two chemically distinct isomers, and, most importantly, interchanges the carbon centers with retention of configuration at the carbinyl carbon center.

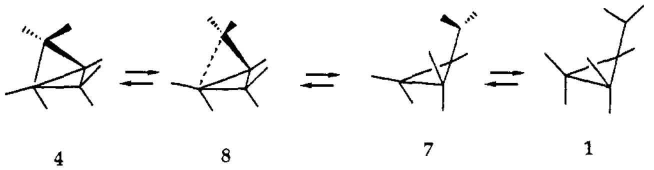

Diagram 8

Proton Rearrangements

Possible pathways for hydrogen scrambling are also of theoretical interest. Experiment has placed an upper limit of 20 kcal/mol for the most facile pathway of hydrogen scrambling within this cationic system.[7c] The lower limit was estimated to be 10 kcal/mol.[6d] Five different pathways have been investigated for hydrogen exchange. The early interest in the homoallyl cations participation led to the investigation of the barrier to rotation of the cation carbon within the homoallyl cation (Diagram 9). (This rearrangement is not likely as **13** would most likely collapse without barrier to the much more stable 1-methylallyl cation.[7d])

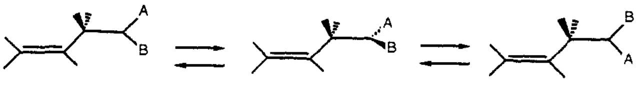

Diagram 9

At MP4SDTQ/6-31G* + ZPE, the energy of the perpendicular homoallylic cation, **13**, was calculated to be 0.8 kcal/mol above the planar form. This pathway is not feasible as it requires >26 kcal/mol from the most stable isomer to the planar form.

The barrier to rotation of the carbinyl carbon within the cyclopropylcarbinyl cation has itself been a subject of some research.[19] The degree of stabilization of the bisected configuration over the perpendicular, **10**, has been estimated from the study of secondary and tertiary cations in stable ion solutions (Diagram 10).[18] At our highest level, the barrier to rotation of the carbinyl carbon is over 35 kcal/mol. This is also beyond the energetic bounds set by experiment.

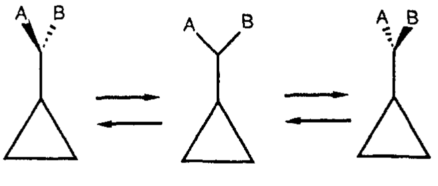

Diagram 10

Another possible mechanism for the interchange of protons is inversion of the cyclobutyl ring. The barrier to inversion is modeled by the relative energy of the planar cyclobutyl cation, **9** (Diagram 11), which is calculated to be 16.11 kcal/mol less stable than **4**.

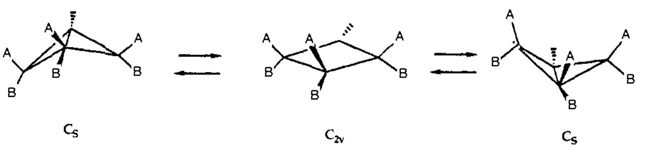

Diagram 11

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[18] A similar prediction of a nonconcerted methylene rotation in the isomerization of butadiene to cyclobutene has been shown to be incorrect. Halgren and Lipscomb found that the nonconcerted motion proposed by Hsu et al. was a fault of the latter's procedure leading to an incorrect description of the interconversion pathway. Our optimizations were not led by any preconceptions of the pathway, but rather merely by a distortion along the negative eigenvector of a *lower level* Hartree–Fock vibrational analysis. Thus while structures **7** and **8** might be slightly off of the lowest energy pathway between **1** and **4**, they give an accurate description of the molecular motion between the two minima. (a) Hsu, K.; Buenker, R. J.; Peyerimhoff, S. D. *J. Am. Chem. Soc.* **1972**, *94*, 5639. (b) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225.

[19] (a) Pittman, C. U., Jr.; Olah, G. A. *J. Am. Chem. Soc.* **1965**, *87*, 2998. (b) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 4939. (c) Deno, N. C.; Liu, J. S.; Turner, J. O.; Lincoln, D. N.; Fruit, R. E., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 3000. (d) Deno, N. C.; Richey, H. G., Jr.; Liu, J. S.; Lincoln, D. N.; Turner, J. D. *J. Am. Chem. Soc.* **1965**, *87*, 4533.

Hydrogen shifts in carbocations are often facile. The 1,3- and 1,2-H shifts were investigated in this system by optimizing the C_s geometries with the hydrogen equidistant between the two carbon atoms involved. The resulting geometries were determined to be transition states by frequency analysis. The relative energies reported in the discussion of the hydrogen transfer mechanisms are from the HF/6-31G** basis set which was used in order to better describe the bridging hydrogens (see Table II). The 1,3-H shift, **12**, corresponds to bicyclobutane protonated on the center bond. This structure was found to be 36.96 kcal/mol above the global minimum, **4**, a corner protonated bicyclobutane (Diagram 12). The 1,2-H shift, **11**, intermediate structure corresponds to a protonated cyclobutene (Diagram 13). By additivity, **11** is estimated to be 16.0 kcal/mol less stable than **4**. (At MP4/6-31G* **11** is 2.65 kcal/mol less stable than the planar **9**, but this need not be involved in the 1,2-H shift process at all.) The relative energy agrees with previous studies of the protonation of bicyclobutanes.[5a,20] Calculations showed that the preferred mode of protonation forms **4**, corner protonated bicyclobutane. This is much more stable than the protonation of the central bond to give **12**, which corresponds to the 1,3-H shift intermediate. This is also in reasonable agreement with the scrambling studies of Roberts et al.[3b]

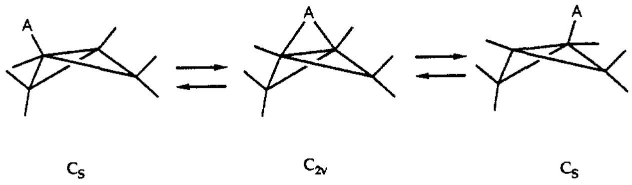

Diagram 12

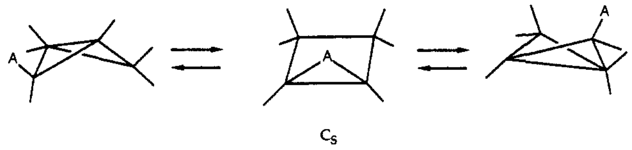

Diagram 13

The relative energies required for the two most likely pathways of hydrogen exchange, cyclobutyl inversion (via **9**) and 1,2-H shift (via **11**) are both within the experimental limits and are estimated to be nearly the same. However, these two mechanisms may be distinguished experimentally. The cyclobutyl inversion exchanges all three methylene hydrogens simultaneously while the 1,2-H shift scrambles single protons. The 1,2-H shift also interchanges the methylene and methine carbon centers where the cyclobutyl inversion does not.

Conclusions

The theoretical energies of the structures explored on the $C_4H_7^+$ potential energy surface can be readily reconciled with the experimental data. Both **1** and **4** are predicted to be minima at the highest levels with very nearly the same energy, **1** being 0.26 kcal/mol more stable than **4**. On the other hand, the observed ^{13}C chemical shifts, the isotopic perturbation results, the calculated chemical shifts, and vibrational analyses predict that **4** is slightly more stable than **1**. A likely pathway of interconversion which leads to 3-fold degeneracy was found, having an activation energy lower than the 2.0 kcal/mol upper-limit deduced from the experimental results. This exchanges the equivalent carbon centers with retention of exo and endo hydrogen regiochemistry. Probable pathways of scrambling for the hydrogens also were explored. Both the 1,2-H shift and the ring-inversion mechanisms are within experimental energy limits for this process. These processes are experimentally distinguishable as the latter results in the exchange of the two types of methylene hydrogens, but the former will exchange all the hydrogens and all the carbons.

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Supplementary Material Available: Tables of zero-point energies and Cartesian coordinates of the $C_4H_7^+$ ion and structures **1**–**12** (17 pages). Ordering information is given on any current masthead page.

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