The $C_3H_7^+$ Cation*

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The $C_3H_7^+$ potential energy surface (PES) is investigated using sophisticated *ab initio* quantum chemical calculations. All structures are fully optimized at the correlated MP2/6-311G(*d*,*p*) level of theory. The $C_3H_7^+$ potential energy surface is characterized by three classes of stationary points, corresponding to the 2-propyl cation, protonated cyclopropane and the 1-propyl cation. While for the first two species conformers representing minimum structures could be identified, no minimum was located for 1-propyl cation. Instead, the two 1-propyl cation structures are saddle points for carbon and of the hydrogen 2-propyl cation scrambling reactions . The global $C_3H_7^+$ minimum is the *chiral*, C_2-symmetric conformer of the 2-propyl cation, which lies 7.2 kcal/mol below the second $C_3H_7^+$ minimum, *i.e.* asymmetrically corner-protonated cyclopropane. In both species, methyl rotation is practically free. The two 1-propyl-cation like saddle points are 19.3 and 20.5 kcal/mol above the global minimum. By comparison of the theoretical and experimental ^{13}C-NMR and IR spectra of 2-propyl cation, the C_2-symmetric structure is identified as the structure present in solution. The preference of the unexpected, twisted geometry of this cation can be attributed to stabilizing hyperconjugation. The proton affinities and heats of formation of the various $C_3H_7^+$ species are computed and compared to the experimental data.

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* Dedicated to Prof. D. E. Sunko on the occasion of his seventieth birthday.
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INTRODUCTION

Carbocations play an important role as reactive intermediates in many key reactions in organic chemistry, such as rearrangements, substitutions and other chemical processes.[1] Detailed knowledge about the structure, the stability and the fate of the carbocation during its short lifetime is therefore of prime importance for an understanding of the underlying reaction mechanisms. While much effort has been directed towards experimental generation and investigation of carbocations and their properties,[2] it is only since the advent of accurate theoretical methods that detailed information about structures and energies of these highly reactive species have become available.[3] It is the synergetic interplay of experimental data gathered from carbocations generated in solution or the gas phase and the results obtained by quantum chemical *ab initio* calculations that offer new insights into the complex carbocation chemistry.

The only $C_3H_7^+$ isomer observable experimentally in solution is the 2-propyl cation (**1**, Scheme 1). This cation is, however, of particular importance since it represents the simplest all-carbon and hydrogen carbocation prepared as a stable species in superacid media. It is generated by destilling 2-chloro- or 2-fluoropropane into a mixture of SbF_5/SO_2ClF at low temperatures.[4] The ^{1}H-NMR of **1** taken by Saunders *et al.* in non-nucleophilic media changes rapidly at temperatures between 0 and 40 °C, indicative of a rapid scrambling of the terminal and central protons.[5] The activation energy for this intramolecular process has been determined to be E_a = 16.4±0.4 kcal/mol. Very similar results were obtained by using 1,1,1-trideuterio-2-propyl cation, which rearranges at –60 °C into the isomeric ions, 1,1,2-trideuterio-, 1,1,3-trideuterio- and 1,2,3-trideuterio-2-propyl cation.[6] The simplest mechanism to explain the hydrogen exchange involves the 1-propyl cation (**2**, Scheme 1) as the central intermediate (mechanism I in Scheme 2). However, this mechanism cannot explain the carbon atom interchange which is seen in [2-^{13}C]-2-propyl cation, which undergoes intramolecular C-scrambling between –90 and –60 °C, The two, very similar, mechanisms which have been put forward in the literature to explain the carbon scrambling both employ protonated cyclopropane (**3**, Scheme 1) as the key intermediate of the rearrangement (mechanisms II and III in Scheme 2). Mechanism II is characterized by corner protonated cyclopropane, which in turn can be reached *via* the 1-propyl cation. Breaking one of the two equivalent CC bonds leads to carbon scrambling. Mechanism III differs from II in the appearance of the edge-protonated cyclopropane as transition
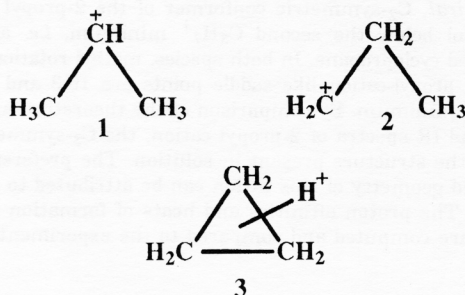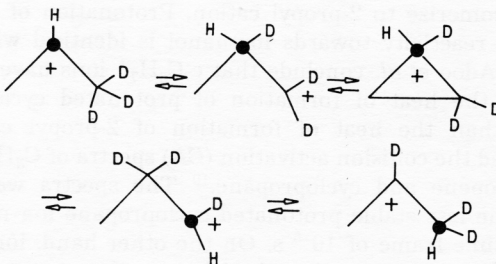

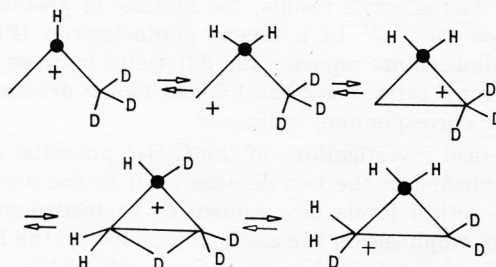Scheme 1. Possible $C_3H_7^+$ structures
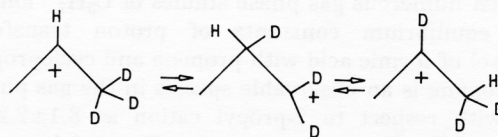
Scheme 2. Reaction mechanisms for carbon and hydrogen scrambling in 2-propyl cation

state or intermediate. In multiple labeling studies it could be shown that hydrogen scrambling occurs 1.5 ± 0.5 times faster than carbon scrambling. Hence, a combination of mechanism I with mechanism II or III, or in other words, 1-propyl as well as protonated cyclopropane, are involved in the scrambling process. By a careful analysis of the deuterium atom scrambling in the propanes formed by quenching of the partially rearranged trideuterated 2-propyl cations, Saunders et al. were able to conclude that the combination of mechanisms II and III is more likely than the combination I and III.[6] Thus, in superacid media corner-protonated cyclopropane should be more stable than the edge-protonated form.[6] In a very recent study, Saunders, Hewett and Kronja reinvestigated the C- and H-scrambling mechanisms in 2-propyl cation. Using ^{13}C and D labeled isopropyl cations and under the assumption that 1-propyl-cation-like structures (which differ in the orientation of the methylene group) are the key intermediates of both mechanisms they concluded the H-scrambling is between 2.1 and 3.1 times faster than C scrambling.[7]

There have been numerous gas phase studies of $C_3H_7^+$ ions. Chong and Franklin investigated the equilibrium constants of proton transfer reactions between protonated methanol of formic acid with propene and cyclopropane.[8] They found that protonated cyclopropane is an observable species in the gas phase and determined its relative stability with respect to 2-propyl cation as 8.1 ± 2.2 kcal/mol. In an ion cyclotron resonance (ICR) spectroscopy study of propyl ions, McAdoo *et al.* showed that while less than 20% of nondecomposing 2-propyl cations undergo isomerization in the time required for the ICR reactions (*ca.* 10^{-3} s) no 1-propyl cations retain their structure.[9] Most isomerize to 2-propyl cation. Protonation of cyclopropane produces $C_3H_7^+$ ions whose reactivity towards methanol is identical with the reactivity of 2-propyl cations. McAdoo *et al.* conclude that c-$C_3H_7^+$ ions have either isomerized into 2-$C_3H_7^+$, or, that the heat of formation of protonated cyclopropane is roughly 7 kcal/mol higher than the heat of formation of 2-propyl cation. McLafferty and coworkers measured the collision activation (CA) spectra of $C_3H_7^+$ ions generated from protonation of propene and cyclopropane.[10] The spectra were identical, thus the isomerization of the less stable protonated cyclopropane ion must occur in less than the experimental time frame of 10^{-5} s. On the other hand, ion-molecule reactions of $C_3H_7^+$ ions at 10^{-2} torr indicate that the lifetime of protonated cyclopropane should be in the order of 10^{-7} s. Attina *et al.* showed through gas phase alkylation experiments that the 1-propyl cation does not play any significant role as a stable isomer, while, in agreement with McLafferty's results, the lifetime of protonated cyclopropane was estimated to exceed 10^{-7} s.[11] In a recent photoelectron (PE) spectroscopy study, Beauchamp and collaborators reported the difference between the heats of formation of 2-propyl and 1-propyl cations as 20.8 ± 1.6 kcal/mol as determined from the ionization energies of the corresponding radicals.[12]

Various theoretical investigations of the $C_3H_7^+$ potential energy surface or parts of it have been published in the two decades prior to the present study. These were carried out at theoretical levels now known to be inadequate. Moreover, all these papers put the main emphasis on the stationary points on the PES and their energetic relationship to each other rather than exploring mechanistic aspects of the experimentally observed rearrangements. The first comprehensive *ab initio* study by Radom, Pople, Buss and Schleyer explored nine $C_3H_7^+$ geometries at HF/4-31G/STO-3G.[13] It was later appreciated that more flexible basis sets were required.[14] In their 1978 paper, Lischka and Köhler used a basis set of DZP quality and the CEPA approximation to account for the first time for electron correlation. They studied the energies of 2-propyl and 1-propyl cation, and corner-, edge- and face-protonated cyclopropane, based on STO-3G optimized geometries.[15] In agreement with all other experimental and theoretical investigations, the 2-propyl cation **1**, was identified as the global minimum on the $C_3H_7^+$ PES. The 1-propyl cation **2** is located 16.5 kcal/mol above **1**, while the edge protonated cyclopropane **3b** is only 2.5 kcal/mol less stable than **1**. Face protonated cyclopropane is predicted to be extremely unstable (99.7 kcal/mol above **1**), while the corner-protonated form **3a** is 5 kcal/mol less favorable than the edge-protonated one.[15] However, neither *ab initio* force constant matrices nor systematic searches for reaction pathways are reported. In their survey of C_1-C_3 carbocations, Raghavachari *et al.* utilized the MP4/6-31G(*d,p*)//HF/6-31G(*d*) level of theory.[16] They found that 1-propyl cation is not a minimum at all on the $C_3H_7^+$ PES, but rearranges spontaneously to corner protonated cyclopropane **3a**. In contrast to Lischka and Köhler's results,[15] the latter structure is predicted to be 0.5 kcal/mol more stable than

the edge protonated isomer **3b** and 8.2 kcal/mol above **1**, in excellent agreement with Chong and Franklin's experimental number.[8] Very similar results for the stability order were obtained by Almlöf *et al.* in a recent MCSCF study.[17] Very recently, Dewar and coworkers reported their MP4*sdq*/6-31G(*d*)//HF/6-31G(*d*) results on protonated cyclopropane.[18] By calculation of the force constant matrix they were able to show that neither edge-protonated **3b** nor corner-protonated **3a** cyclopropane represent a true minimum on the C$_3$H$_7$$^+$ PES. Both structures exhibit one negative eigenvalue and thus represent saddle points rather than minima. They identified an unsymmetrical species **3c**, not considered before, as the only genuine minimum for protonated cyclopropane. The energy differences between the various protonated cyclopropane structures are, however, very small (less than 1 kcal/mol). In their paper the authors speculate that this result for protonated cyclopropane may also make an unsymmetrical geometry more likely for the much debated structure of the 2-norbornyl cation. This, however, has recently shown not to be the case. The gas phase structure of the 2-norbornyl cation is without doubt symmetrical.[19] In two recent communications we have discussed some aspects of the C$_3$H$_7$$^+$ potential surface[20] and in particular the equilibrium structure of the 2-propyl cation.[21]

The aim of the present paper is to give an accurate, detailed and comprehensive theoretical description of the chemical relevant parts of the ground state potential energy hypersurface of the C$_3$H$_7$$^+$ carbocationic system. Using sophisticated quantum chemical *ab initio* techniques, employing large one-particle basis sets and explicit consideration of electron correlation effects (also in the geometry determination), we will address the following questions:

What are the exact structures of the stationary points, *i.e.* 2-propyl cation, protonated cyclopropane and 1-propyl cation? Which are minima and which saddle points?

What is their energetic relationship?

Which reaction paths between different isomers can explain the experimentally observed C and H scrambling?

The present work should be considered as an extension of our previous systematic theoretical investigations on small, prototype carbocations, like, *e.g.* C$_1$–C$_3$,[16] C$_2$H$^+$,[22] C$_4$H$_7$$^+$,[23] C$_4H_9$$^+$,[24] C$_5H_7$$^+$,[25] C$_5H_9$$^+$,[26] C$_5H_{11}$$^+$,[27] and the 2-norbornyl cation,[19] which we reported recently.

COMPUTATIONAL METHODS

Standard but high levels of *ab initio* quantum chemical calculations have been employed using the GAUSSIAN 86[28] and GAUSSIAN 90[29] program packages as installed on the Convex and CDC Cyber computers in Erlangen and IBM ES/3090 computers equipped with Vector Facility at the IBM Almaden research Center and at IBM Germany's Computing Center in Düsseldorf. All geometries have been fully optimized within the specified point group symmetry using the 6-311G *sp*-basis set, augmented by *p*- and *d*-type functions on hydrogen and carbon, respectively (*i.e.* 6-311G(*d,p*)). The effects of dynamical electron correlation have been accounted for through Møller-Plesset perturbation theory terminated at second order, correlating all electrons (*i.e.* MP2(full)/6-311G(*d,p*)). To characterize the stationary points as minima or saddle points and to correct the energies for zero point vibrational energy (ZPE), and to simulate the IR spectra, the harmonic vibrational frequencies and IR intensities have been

obtained at the same theoretical level, or, in some cases, at the somewhat less flexible MP2(full)/6-31G(d) level. To allow for more accurate energy comparisons, single point energy calculations at the optimized geometries employing full fourth order Møller-Plesset perturbation theory for the valence electrons and the 6-311G(d,p) basis set have been carried out. Thus, in standard notation our final level of theory is MP4$sdtq$(fc)/6-311G(d,p)//MP2(full)/6-311G(d,p) + ZPE. All data given in the text will refer to this level, if not otherwise noted. For a detailed description of the quantum chemical methods and basis sets used, the reader is referred to Ref. 3c. The ^{13}C-NMR chemical shifts have been theoretically predicted using the IGLO method developed by Schindler and Kutzelnigg.[30]
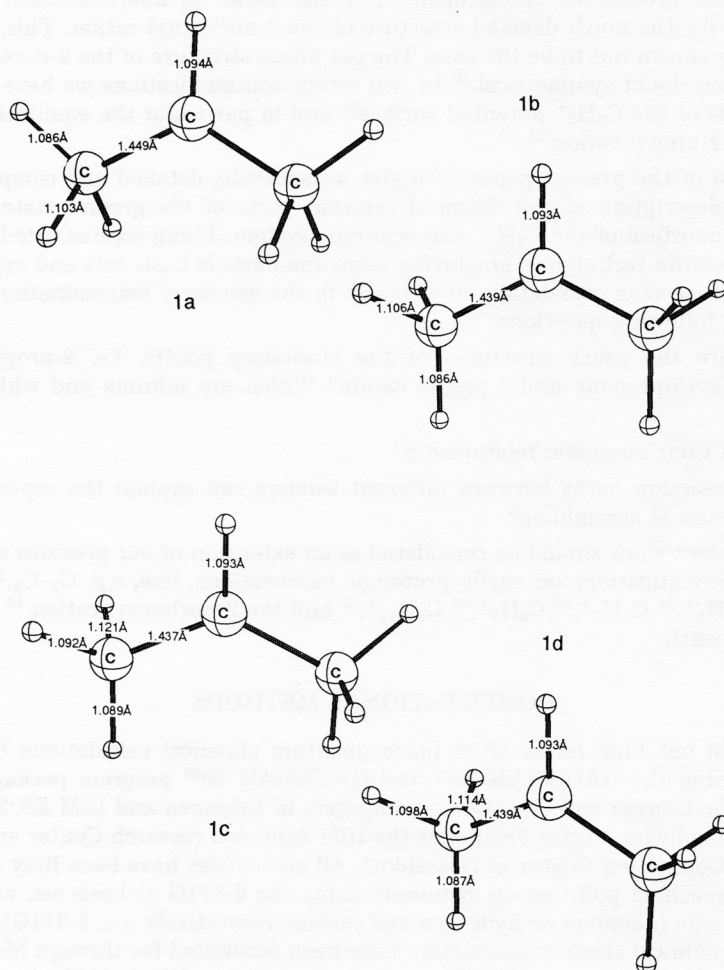

Figure 1. Optimized geometries, bond lengths in Å

The optimized geometries of the structures discussed are displayed in Figure 1. Total and relative energies are collected in Tables I and II, respectively. Table III compares the theoretically predicted ¹³C chemical shifts with the experimental data, while Table IV contains the harmonic frequencies and IR intensities of the two stable C₃H₇⁺ species, computed at MP2(full)/6-31G**.
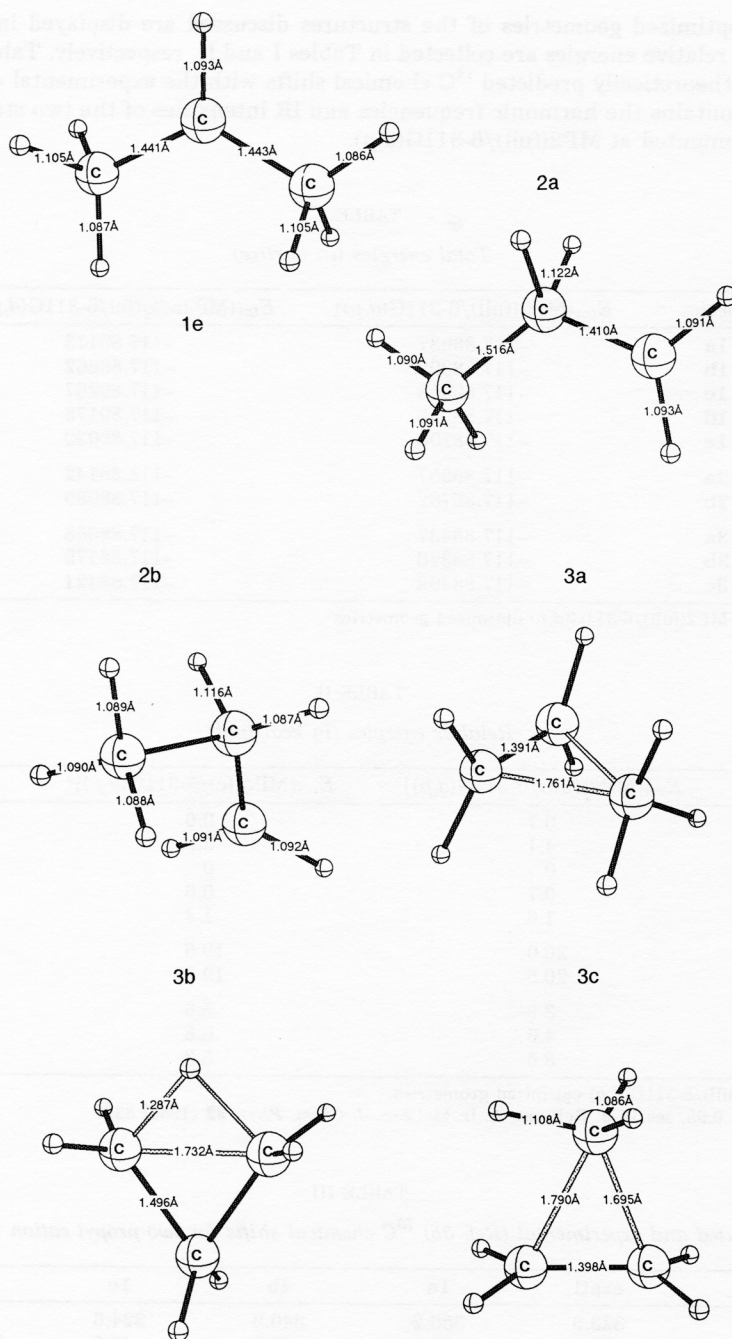

Figure 1, continued. Optimized geometries, bond lengths in Å

The optimized geometries of the structures discussed are displayed in Figure 1. Total and relative energies are collected in Tables I and II, respectively. Table III compares the theoretically predicted ^{13}C chemical shifts with the experimental data, while Tabe IV contains the harmonic frequencies and IR intensities of the two stable $C_3H_7^+$ species, computed at MP2(full)/6-311G(d,p).

TABLE I

Total energies (in hartree)

Species	E_{tot}(MP2(full)/6-311G(d,p))	E_{tot}(MP4$sdtq$(fc)/6-311G(d,p))[a]
1a	−117.88937	−117.89173
1b	−117.88392	−117.88662
1c	−117.89053	−117.89267
1d	−117.88945	−117.89178
1e	−117.88795	−117.89039
2a	−117.85857	−118.86142
2b	−117.85782	−117.86089
3a	−117.88437	−117.88368
3b	−117.88320	−117.88179
3c	−117.88499	−117.88421

[a] at MP2(full)/6-311G(d,p) optimized geometries

TABLE II

Relative energies (in kcal/mol)

Species	E_{rel}[MP2(full)/6-311G(d,p)]	E_{rel}[MP4(fc)/5-311G(d,p)][a]	+ZPE[b]
1a	0.7	0.6	0.3
1b	4.1	3.8	3.6
1c	0	0	0
1d	0.7	0.6	0.4
1e	1.6	1.4	1.3
2a	20.0	19.6	19.3
2b	20.5	19.9	20.5
3a	3.9	5.6	7.3
2b	4.6	6.8	8.6
3c	3.5	5.3	7.2

[a] at MP2(full)/6-311G(d,p) optimized geometries,
[b] scaled by 0.95, see D. J. DeFrees, A. D. McLean, *J. Chem. Phys.* **82** (1985) 333.

TABLE III

Computed and experimental (Ref. 35) ^{13}C chemical shifts for two propyl cation isomers

Atom	exptl	**1a**	**1b**	**1c**	**1d**
CH	323.9	356.2	340.9	324.6	346.4
CH_3	53.8	38.2	42.7	44.5	40.3, 42.7

Structure **1c** has almost identical values as structure **1a** and has not been included explicitly

TABLE IV (A and B)

Computed IR spectra of 1c and 3c

A – 2-propyl cation, C_2 symmetry (1c)				B – asymmetrically corner protonated cyclopropane, C_s symmetry (3c)			
ν	ν [scld][a]	symmetry	I	ν/cm^{-1}	ν/cm^{-1} [scld][a]	symmetry	I km mol^{-1}
183	174	B	7.9	176	167	A''	4.3
247	235	A	8.6	401	381	A'	60.5
426	405	A	1.1	530	504	A'	17.9
597	567	A	2.2	825	784	A''	0.4
604	574	B	127.8	872	828	A'	23.5
952	904	A	0.2	899	854	A''	2.7
982	933	B	1.7	1061	1008	A''	2.9
1087	1042	B	71.5	1118	1062	A''	0.0
1228	1166	A	10.0	1179	1120	A'	9.1
1269	1206	B	8.2	1184	1125	A'	15.6
1322	1256	A	15.7	1250	1188	A''	0.7
1326	1260	B	162.6	1328	1262	A'	12.4
1368	1300	B	9.7	1357	1289	A'	3.2
1378	1309	A	15.9	1426	1355	A''	18.3
1467	1394	B	44.5	1470	1397	A'	6.1
1508	1433	A	12.0	1510	1435	A'	17.2
1570	1492	B	66.2	1591	1511	A'	0.8
2896	2751	B	256.1	3019	2868	A'	62.7
2914	2768	A	10.0	3176	3017	A'	17.3
3142	2985	A	0.1	3193	3033	A'	12.8
3143	2986	B	31.8	3211	3050	A'	10.1
3188	3029	A	1.3	3291	3126	A''	18.5
3242	3080	B	9.2	3304	3139	A''	2.0
3242	3080	A	16.1	3327	3161	A''	36.3

[a] scaled by 0.95. See D. J. DeFrees, A. D. McLean, *J. Chem. Phys.* **82** (1985) 333.

ENERGIES AND STRUCTURES

2-Propyl Cation

The 2-propyl cation **1** is the only $C_3H_7^+$ isomer that can be generated and detected in solution and there is no doubt that it represents the global minimum on the $C_3H_7^+$ PES. In prior theoretical studies, two different structures, both with C_{2v} point group symmetry, have been considered (**1a** and **1b**). Both structures suffer from an unfavorable steric repulsion of the methyl hydrogens. We find that **1a** is more stable by 3.3 kcal/mol. However, the force constant matrices, computed at MP2(full)6-311G(d,p) reveal that neither structure is a minimum on the PES. Both are characterized by two negative eigenvalues with imaginary frequencies of 201i (A_2) and 81i cm^{-1} (B_1) **1a**, and 361i (B_1) and 268i cm^{-1} (A_2) **1b**, respectively. Thus, these 2-propyl cation structures are not even transition structures but have to be considered as chemically irrelevant second order saddle points. Symmetry reduction from C_{2v} to C_2 leads to a stationary point which is indeed a minimum with a positive definite force constant matrix **1c**.[21] The most interesting aspect of this structure, which is only marginally more stable than the C_{2v} form **1a**, is that it is chiral. It thus contradicts the current belief that

acyclic classical carbocations are inherently achiral. This result has recently been confirmed by MP2-R12 calculations by Klopper and Kutzelnigg.[31] A fourth 2-propyl cation structure is the C_s symmetric conformer **1d**, with the mirror plane bisecting the CCC angle. **1d** has one negative eigenvalue in the force constant matrix and represents the saddle point for conversion of **1c** in its enantiomer. The barrier height of the methyl rotation is, however, very small. After inclusion of ZPE corrections a value of 0.3 kcal/mol has been obtained. Thus, there is virtually free methyl rotation in 2-propyl cation and its chirality does not have any chemical significance. Finally, a second C_s symmetric conformer with the mirror plane defined by the three carbon and the central hydrogen atom could be located **1e**. Also **1e** represents a rotational transition structure for the methyl groups, but is 0.9 kcal/mol less stable than **1d**.

In **1c**, the two methyl groups are rotated clockwise and counterclockwise to each other in order to maximize the hyperconjugative stabilization of the cation. One hydrogen atom on each methyl group is almost perfectly aligned parallel with the formally empty p_z atomic orbital on the central, cationic carbon atom (Scheme 3). Electron donation from this C–H bond into the empty orbital leads to the geometrical consequences typical for hyperconjugation, *i.e.* elongation of one of the C–H bond distances from 1.09 Å to 1.12 Å and a decrease of the corresponding HCC bond angle from the standard sp^3 value of 109.4° to 97° caused from the bending of the hyperconjugating methyl hydrogen towards the formal cationic center. Geometrical distortions of this type, caused by hyperconjugative interaction, are a general feature of carbocationic structures and have already been found in many instances.[1d,21,26,27] The elongation of the C–H bond with concomitant bending towards the cationic carbon atom can also be considered as the onset of hydrogen bridging. In this sense, even a carbocation as simple as 2-propyl cation is not fully »classical«.
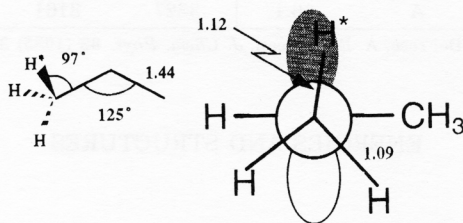
Scheme 3. Hyperconjugation in **1c**

Protonated Cyclopropane

The structure of protonated cyclopropane **3** has not been fully established.[32] The only structurally relevant experimental information favors the corner-protonated form over the edge-protonated one.[6] As described in the Introduction, the various prior theoretical investigations disagree on the minimum energy structure of **3**. However, the most recent study, performed at MP4sdq/6-31G(d)//HF/6-31G(d) points to an unsymmetrical structure **3c** as the most likely candidate for the lowest energy protonated cyclopropane arrangement.[18] Our calculations, at a considerably higher theoretical level, substantiate this conclusion. Among the three structural alternatives considered, *i.e.* symmetrically corner-protonated **3a**, edge-protonated **3b** and unsymmetrically

corner-protonated cyclopropane **3c**, the latter is found to be the most stable one. However, the distortion from the C$_{2v}$ structure **3b** is less pronounced at the correlated MP2/6-311G(d,p) level than in Dewar's original Hartree-Fock geometry of this species.[18] Symmetrically corner-protonated cyclopropane **3a** is only a few tenths of a kcal/mol less stable than **3c**. However, **3a** is not a minimum but rather represents the transition structure for methyl rotation in **3c**, which is virtually free. 1.4 kcal/mol above **3c**, we localized the geometry for edge-protonated cyclopropane **3b**. In their previous theoretical study, Raghavachari *et al.* found at the rather modest HF/3-21G level this species is not a minimum, but a saddle point.[16] However, at the MP2(full)/6-311G(d,p) level of theory **3** is computed to have a positive definite force constant matrix, representing a shallow minimum on the C$_3$H$_7$$^+$ PES. We investigated this discrepancy between these two theoretical levels further by optimizing the geometry and computing the force constant matrix of this structure employing a variety of basis sets, with and without the inclusion of electron correlation. It turns out that **3b** is indeed a transition state at the Hartree-Fock level with all basis sets used. Only after electron correlation effects are taken into account and a basis with d-type polarization functions on carbon is employed, the lowest frequency of **3b** is no longer imaginary but real. However, the true nature of edge-protonated cyclopropane cannot be established conclusively, since the saddle point connecting **3b** with the lower energy conformer **3c** is almost energetically identical to **3b** and becomes even lower in energy when zero-point energy corrections are applied. The central conclusion is that the C$_3$H$_7$$^+$ PES around protonated cyclopropane is extremely flat and complete hydrogen scrambling in this species through methyl rotation and H-migration from one carbon to another is associated with very low barriers. The theoretically predicted energy difference between the global minimum, 2-propyl cation **1c** and the unsymmetrical corner protonated cyclopropane **3c** amounts to 7.2 kcal/mol, which is in good agreement with the experimental result of 8.1±2.2 kcal/mol of Chong and Franklin.[8]

1-Propyl Cation

Despite a careful search, we could not locate a minimum structure corresponding to the 1-propyl cation **2** on the C$_3$H$_7$$^+$ PES. This is in agreement with the experience gained from other small primary cations, which are known to be very unstable and usually tend to rearrange to more stable isomers without activation barrier.[33] We did, however, find two stationary points for the 1-propyl cation: **2a** point group symmetry C$_s$ and **2b**, point group symmetry C$_1$. Both structures are geometrically very similar and differ primarily only in the conformation of the cationic methylene group. **2a** and **2b** are also of similar stability, 19.3 and 20.5 kcal/mol above the global minimum, respectively. Diagonalization of the force constant matrix gave one negative eigenvalue and thus one imaginary frequency for both structures indicating that **2a** as well as **2b** represent transition structures. Analysis of the normal modes related to the imaginary frequencies revealed that the C$_s$ symmetric, bisected structure **2a** is the transition structure for hydrogen migration from 2-propyl cation. Thus the process **1c** → **2a** results in hydrogen, but not in carbon scrambling. On the other hand, **2b** is the saddle point for the conversion of protonated cyclopropane **3c** into the global minimum, chiral 2-propyl cation **1c**. This process occurs by widening of the C$_1$C$_2$C$_3$ angle of **3c** with a concomitant rotation of the C$_1$ methylene group until the 1-propyl cation structure **2b** is reached. A hydrogen then migrates from the central carbon without activation barrier to yield **1c**. In contrast to the former process, the sequence **1c** → **2b** →

→ **3c** (and from here further rearrangements *via* the various protonated cyclopropanes, *vide supra*) leads to hydrogen and carbon exchange.

Other Structures

We carefully searched for other stable $C_3H_7^+$ minima. In particular we looked for possible hydrogen bridged structures corresponding to protonated propene, in analogy to the H-bridged structures known, *e.g.*, for protonated ethylene[16] or 2-butene.[24] We were only able to locate such a structure at 3-21G, but this did not survive at higher levels. A flat potential energy surface, but no further stationary point was found on MP2/6-31G*d*) optimization.

^{13}C-NMR Chemical Shift Calculations of 2-Propyl Cation[21]

One of the major experimental sources of information for reactive, short-lived species like carbocations are proton- and ^{13}C-NMR spectra. Many general structural features and stabilities towards rearrangement can be deduced.[4,5,6,34] The theoretical prediction of NMR spectra has for a long time played a minor role, *e.g.* for the investigation of such species, due to the algorithmic problems (most of all the gauge dependence of the magnetic properties due to basis set truncation) inherent to the computation of magnetic properties. However, recent developments by Kutzelnigg,[30] Pulay,[35] and others have led to new, efficient and accurate theoretical methods for computing chemical shifts.[36] The theoretical determination of magnetic properties at a level equivalent to that employed to compute structures and energies afford an excellent opportunity for a coherent comparison between experimental and theoretical results. It turned out that the ^{13}C chemical shifts depend very strongly on the geometry and that a comparison between experiment and theory offers a new and sensitive probe for structure determination.[1d,23b,24,26,27] In prior investigations we successfully used this approach to identify the minimum structure of, *e.g.* the cyclopentyl cation[26] and 2-butyl cation[24] or to distinguish between different conformers of the *t*-butyl cation.[24] The technique we are employing for these calculations is the IGLO (Individual Gauge for Localized Orbitals) method of Schindler and Kutzelnigg, which is based on gauge dependent orbitals.[30]

The ^{13}C chemical shifts of 2-propyl cation have been determined experimentally by Olah and Donovan.[34] In order to substantiate our result that the global minimum for 2-propyl cation is the chiral, C_2-symmetric conformer **1c**, we computed the ^{13}C chemical shifts for all five stationary points located for the 2-propyl ion.[37] The data shown in Table III speak for themselves: Only the chemical shifts computed for **1c** agree with experiment, while the other four conformers differ considerably from Olah and Donovan's results. Thus, it can be concluded that structure **1c** is indeed the 2-propyl cation species generated in super acid media.[21]

The smaller ^{13}C chemical shift for the cationic carbon atom for **1c** compared to the other 2-propyl cation conformers is a direct consequence of the stabilizing hyperconjugative interaction already described above to rationalize the preference of a twisted, C_2-symmetric geometry of this cation. The partial hydrogen bridging in **1c** leads to an enhanced delocalization of the positive charge away from the formally charged central carbon atom and thus results in a smaller degree of deshielding (Scheme 3).

Vibrational Spectra of the 2-propyl Cation

Infrared and Raman spectroscopy are also important spectroscopic means to elucidate geometries and related properties of molecules. The theoretical simulation of the IR and Raman spectra through calculation of the harmonic frequencies and the corresponding IR intensities using the available programs is straightforward and is only limited by the computational resources available. However, experimental information about the vibrational spectra of carbocations has been very scarce. The first IR spectroscopic study of 2-propyl cation was performed by Olah et al..[4] They obtained the IR spectra in superacid media, however, with only low resolution. Very recently, Sunko and coworkers developed a new promising experimental technique, which allows the study of infrared spectra of carbocations in cryogenic SbF_5 matrices.[38] Among the first applications of this method was a comparison of computed and experimentally obtained IR spectra of the 2-norbornyl cation which demonstrated the usefulness of this combined approach to help identifying the minimum geometry of such species.[19b] Similarly, the 2-butyl[24b] and cyclooctyl[39] cation could be shown to prefer symmetrically H-bridged structures.

We used the modified version of Vančik and Sunko[38] to reinvestigate the 2-propyl cation IR spectrum. The cation was generated from cocondensation of 12 mg of 2-propylchloride and 300 mg of SbF_5 on a cold NaCl disc at –160 °C. When the solid matrix was warmed to –50 °C, the spectrum of the 2-propyl cation developed (Figure 2). Olah's spectrum displayed only six relevant signals as well as impurity peaks. Our matrix spectrum is of considerable higher quality and has many more signals. Two striking peaks, already prominent in Olah's spectrum are found at 2739 and 1263 cm^{-1}. They correspond to the MP2/6-311G(d,p) frequencies computed to be very intense (2751 cm^{-1}, 256,1 km/mol and 1260 cm^{-1}, 162.6 km/mol, scaled by 0.95). Normal mode analysis shows that the 2738 cm^{-1} vibration is due to the stretching of C–H bonds weakened by hyperconjugation. The 1263 cm^{-1} peak is a HCH deformation. As first pointed out by Vančik and Sunko[38] with regard to the 2775 cm^{-1} vibration of the
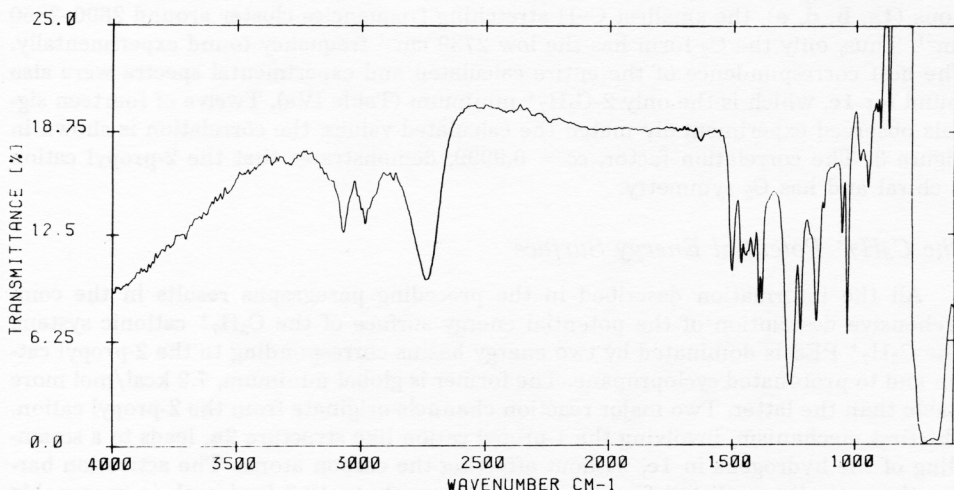

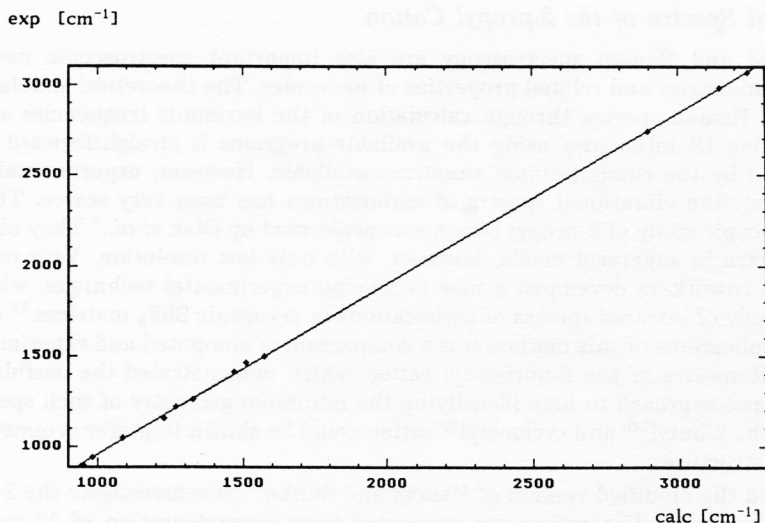Figure 2. Experimental IR spectrum of 2-propyl cation

exp [cm^{-1}]

Figure 3. Correlation of experimental and computed IR spectrum for the 2-propyl cation

methyl cyclopentyl cation, the IR frequencies show the degree of hyperconjugative bond weakening by the magnitude of the decrease of the C–H stretching frequencies. For example, the characteristic C–H stretching of the *t*-butyl cation is only shifted to 2840 cm^{-1}, since hyperconjugation is less effective in tertiary cations than in the secondary 2-propyl cation. When symmetrically H-bridged ions are present, the corresponding frequencies are much lower, *ca.* 2000–2100 cm^{-1}.[24b,39]

Frequency calculations were carried out also for all the other 2-propyl conformations (**1a, b, d, e**), the smallest C–H stretching frequencies cluster around 2800–2850 cm^{-1}. Thus, only the C_2 form has the low 2739 cm^{-1} frequency found experimentally. The best correspondence of the entire calculated and experimental spectra were also found for **1c**, which is the only 2-$C_3H_7{}^+$ minimum (Table IVa). Twelve of fourteen signals observed experimentally match the calculated values, the correlation is shown in Figure 3. The correlation factor, *cc* = 0.9999, demonstrates that the 2-propyl cation is chiral and has C_2 symmetry.

The $C_3H_7{}^+$ Potential Energy Surface

All the information described in the preceding paragraphs results in the comprehensive description of the potential energy surface of the $C_3H_7{}^+$ cationic system. The $C_3H_7{}^+$ PES is dominated by two energy basins corresponding to the 2-propyl cation and to protonated cyclopropane. The former is global minimum, 7.2 kcal/mol more stable than the latter. Two major reaction channels originate from the 2-propyl cation. The first mechanism, involving the 1-propyl cation like structure **2a**, leads to a scrambling of the hydrogens in **1c**, without affecting the carbon atoms. The activation barrier theoretically predicted for this process amounts to 19.3 kcal/mol, in reasonable agreement with the experimental estimate of 16.3±0.4 kcal/mol determined in non-nucleophilic media by Saunders *et al.*.[6] The other reaction channel is also charac-
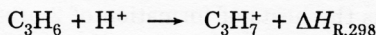
terized by a 1-propyl cation transition structure **2b**, differing in conformation from **2a**. After surpassing the barrier of 20.5 kcal/mol associated with **2b**, complete scrambling of all carbon as well as hydrogen atoms in the molecule is achieved through the various protonated cyclopropane cation structures. In accord with the experimental observation that H-scrambling is somewhat faster than C-scrambling,[6,7] the latter process has a slightly higher activation barrier than the former (20.5 kcal/mol for **2b** and 19.3 kcal/mol for **2a**, respectively).

Relative Stabilities of Propyl Cations and Proton Affinities of Propene and Cyclopropane

All experimental and theoretical investigations agree that the 2-propyl cation is the most stable structure. The most reliable experimental determination of heats of formation of propyl cations seems to be the recent PE spectroscopy study of Beauchamp and coworkers and the revised data in Ref. 42, which are given in the following.[12] They determined that heat of formation of the 2-propyl cation from the adiabatic ionization energy of the 2-propyl radical (7.36±0.02 eV) and the heat of formation of the radical (22.3 kcal/mol) as ΔH_f (2-propyl cation) = 190.9 kcal/mol. Using the same technique, the heat of formation of the 1-propyl cation can be obtained. However, one has to keep in mind that this cation does not represent a minimum on the potential energy surface. The observed photoelectron process is limited by the accessible Franck-Condon region and thus the measured ionization energy refers to a 1-propyl like structure, but not necessarily to the lowest energy conformation.[40] Beauchamp and coworkers give a value of ΔH_f (1-propyl cation) = 211 kcal/mol (with ΔH_f (1-propyl radical = 24.0 kcal/mol and IE (1-propyl radical) – 8.09±0.02 eV). Thus, the difference between the heats of formation of 1-propyl and 2-propyl cations is 20.1 kcal/mol as determined from the photoelectron data. This result agrees well with our theoretically predicted stability difference of 19.3 kcal/mol (and is also larger than the superacid H-scrambling barrier E_a = 16.4 kcal/mol[5,6]). Due to uncertainties of the heat of formation of the parent radical, no heat of formation was reported for the third $C_3H_7^+$ species, *i.e.* protonated cyclopropane.[12] The heat of formation of the latter cation was determined by Chong and Franklin, as described in the Introduction to be 8.1±2.2 kcal/mol higher than that the of 2-propyl cation.[8] Also this result is in excellent agreement with the computed energy difference of 7.2 kcal/mol. Adding the 8.1 kcal/mol energy difference to the experimental heat of formation of the 2-propyl cation (190.9 kcal/mol) determined in the PE spectroscopy experiment, one arrives at a heat of formation of 198.5 kcal/mol for protonated cyclopropane.

The proton affinities at 298.15 K of propene and cyclopropane, respectively, have been theoretically predicted using the following equation.[41]

$$C_3H_6 + H^+ \longrightarrow C_3H_7^+ + \Delta H_{R,298}$$

$$-PA = \Delta H_{R,298} = \Delta E_{elec} + \Delta E_{vib,298} + \Delta E_{rot,298} + \Delta E_{trans,298} + \Delta(pV)^{298}$$

Standard statistical mechanics formulas and scaled harmonic vibration frequencies computed at MP2/6-311G(d,p) have been used to determine $\Delta E_{vib,298}$. The rotational and translational terms have been computed classically and amount to $\Delta E_{rot,298}$ = 0 and $\Delta E_{trans,298}$ = 3/2 RT –0.9 kcal/mol. $\Delta(pV)^{298}$ was computed using the ideal gas law,

and is for the protonation reaction $-RT$, *i.e.* 0.6 kcal/mol. For propene, we arrive at a PA of 177.8 kcal/mol, while the PA of cyclopropane is computed as 178.0 kcal/mol. These data can be compared with the currently accepted experimental values of 179.5±0.8 and 179.8 kcal/mol, for propene and cyclopropane, respectively.[42] Using these values and the known experimental heats of formation of H^+ (365 kcal/mol[43]), propane (4.9 kcal/mol[44]) and cyclopropane (12.7 kcal/mol[44]) we compute $\Delta H_{f,298}$ for 2-propyl cation and protonated cyclopropane as 192.1 and 199.7 kcal/mol as compared to the experimental results of 189.6 and 197.7 kcal/mol, respectively (*vide supra*).

SUMMARY

Using high levels of *ab initio* molecular orbital theory, the $C_3H_7^+$ cation has been investigated. A complete description of the relevant parts of the $C_3H_7^+$ potential energy surface, characterizing the minimum as well as transition structures of the important isomerization reactions is been given. The following main conclusions emerge from this study:

1. The most stable $C_3H_7^+$ cation isomer is the 2-propyl cation. It prefers a chiral (C_2 point group) ground state geometry, which can be attributed to hyperconjugative stabilization. The methyl rotation barriers are very small, less than 1 kcal/mol.

2. Protonated cyclopropane is a second, stable $C_3H_7^+$ isomer. In its lowest energy conformation it assumes an asymmetrically edge protonated geometry, as already pointed out by Dewar and coworkers. This structure is 7.2 kcal/mol above the 2-propyl cation minimum. Methyl rotation is practically free, and also hydrogen migration around the ring has a low barrier of merely 1.4 kcal/mol.

3. There is no minimum structure corresponding to a primary 1-propyl cation. However, two different stationary points have been located, which differ in the degree of rotation of the CH_2^+ group. Both represent transition structures for H- and C-scrambling reactions and are 19.2 and 20.5 kcal/mol less stable than the 2-propyl cation, respectively.

4. The potential energy surface constructed from these information allows an interpretation of the experimentally observed hydrogen and carbon scrambling reactions. One reaction channel only leads to hydrogen equilibration, while another scrambles all atoms in the molecule. The former has the lower barrier, in agreement with the experimental finding that H-scrambling is slightly faster than C-scrambling.

5. The comparison of theoretically predicted ^{13}C-NMR and IR spectra of the 2-propyl cation with the available experimental data allows an unambiguous identification of the minimum structures and demonstrates the power of such combined theoretical/experimental approaches.

6. The compound proton affinities of propene (177.8 kcal/mol) and cyclopropane (178.0 kcal/mol) as well as the heats of formation of 2-propyl cation (192.1 kcal/mol) and protonated cyclopropane (199.7 kcal/mol) are in excellent to good agreement with experiments (PA(propene) = 179.5±0.8 kcal/mol, PA(cyclopropane) = 179.8 kcal/mol, ΔH_f (2-propyl cation) = 190.9 kcal/mol, ΔH_f (protonated cyclopropane) = 198.5 kcal/mol).

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SAŽETAK

$C_3H_7^+$ – kation

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Istražena je ploha potencijalne energije kationa $C_3H_7^+$ primjenom vrlo složenih kvantno-kemijskih proračuna: sve strukture potpuno su optimizirane postupkom MP2/6-311G(*d,p*). Ploha potencijalne energije karakterizirana je trima stacionarnim točkama koje odgovaraju 2-propil-kationu, protoniranom ciklopropanu i 1-propil-kationu. Razmotrena su njihova strukturna i energijska svojstva kao i protonski afiniteti. Usporedba teorijskih i eksperimentalnih ^{13}C NMR i IR spektara 2-propil-kationa pokazuju da struktura koja se pojavljuje u otopini ima simetriju C_2.