Carbocations

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Structural Isomerization of the Gas-Phase 2-Norbornyl Cation Revealed with Infrared Spectroscopy and Computational Chemistry**

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Abstract: *In an attempt to produce the 2-norbornyl cation ($2NB^+$) in the gas phase, protonation of norbornene was accomplished in a pulsed discharge ion source coupled with a supersonic molecular beam. The $C_7H_{11}^+$ cation was size-selected in a time-of-flight mass spectrometer and investigated with infrared laser photodissociation spectroscopy using the method of "tagging" with argon. The resulting vibrational spectrum, containing sharp bands in the C–H stretching and fingerprint regions, was compared to that predicted by computational chemistry. However, the measured spectrum did not match that of $2NB^+$, prompting a detailed computational study of other possible isomers of $C_7H_{11}^+$. This study finds five isomers more stable than $2NB^+$. The spectrum obtained corresponds to the 1,3-dimethylcyclopentenyl cation, the global minimum-energy structure for $C_7H_{11}^+$, which is produced through an unanticipated ring-opening rearrangement path.*

The 2-norbornyl cation ($C_7H_{11}^+$; $2NB^+$) is the most famous and controversial carbocation.[1,2] On the basis of unusual solvolysis reaction rates and products of 2-*exo*- and 2-*endo*-norbornyl derivatives,[3–8] Winstein proposed a symmetrically bridged nonclassical structure for the ion intermediate.[5] In sharp disagreement, Brown favored rapidly equilibrating classical structures.[9] This dispute continued vehemently for decades. Experiments on $2NB^+$ under "stable ion" conditions in "superacid" media supported the non-classical structure, as did theory at ever-more sophisticated levels.[10–21] Notably, Saunders demonstrated deuterium isotope effects on the ^{13}C NMR spectra showing no rapid equilibration,[14] and Yannoni's cryogenic (5 K) ^{13}C NMR spectra showed a static symmetrically bridged structure.[15] However, proponents of the classical structure argued that these results were not definitive because of the long NMR time scale. Recently, the long-sought X-ray crystal structure of $2NB^+$ was obtained, confirming its nonclassical structure in the condensed phase.[22] Nevertheless, questions remain about the nature of this ion in the gas phase. Is the isolated ion intrinsically stable, or is it stabilized by the counter ions and solvation in the superacid media? Although aspects of its chemistry have been studied by mass spectrometry,[23–27] no gas-phase spectroscopy of $2NB^+$ has been reported. Our objective was to measure the infrared spectrum of the mass-selected $C_7H_{11}^+$ ion and to determine its structure from the vibrational patterns by comparison to the predictions of theory. To our surprise, the structure of $C_7H_{11}^+$ obtained under our conditions is not that of $2NB^+$, but instead corresponds to a much more stable rearranged ion. This rearrangement and the unexpected $C_7H_{11}^+$ isomer are the subjects of this paper.

Previous mass spectrometry of $2NB^+$ explored its reactions and collisional dissociation behavior.[23–27] Fragmentation patterns of $C_7H_{11}^+$ produced by different methods are similar, and energetic thresholds are consistent with the thermochemistry expected for $2NB^+$.[27] However, rearrangements are common in ion fragmentation and these experiments did not establish actual ion structures. Although $2NB^+$ is well-known in the condensed phase, it is not generally recognized that it is not the $C_7H_{11}^+$ global energy minimum. Computational studies have explored some $C_7H_{11}^+$ isomers, but there has been no comprehensive study of the potential energy surface, and no studies of this system at higher levels of theory.[20,28,29] We compared the experimental infrared spectrum of the $C_7H_{11}^+$ isomer produced by norbornene protonation with those predicted computationally for various isomers. Theory finds that several of these are more stable than $2NB^+$, but only the $C_7H_{11}^+$ global energy minimum gives a good match with the experiment.

The infrared spectrum of our $C_7H_{11}^+$ isomer, obtained by photodissociation of argon tagged species,[30] is shown in Figure 1. $C_7H_{11}^+Ar$ was produced in a discharge of norbornene and H_2 in argon; abundant H_3^+ acts as the protonating agent. After mass selection, the spectrum was recorded as the wavelength dependent yield of the $C_7H_{11}^+$ photofragment. It contains a strong broad band at 2910 cm^{-1} in the C–H stretching region and weaker absorptions at higher frequencies. Sharper structures characterize the fingerprint region, with bands at 995, 1230, 1333, 1389, 1421, 1482 cm^{-1}, and the most prominent peak at 1525 cm^{-1}. Notably, this spectrum does not correspond to that predicted for $2NB^+$ (Figure 1, bottom) at the MP2/cc-pVTZ level of theory. Likewise, it

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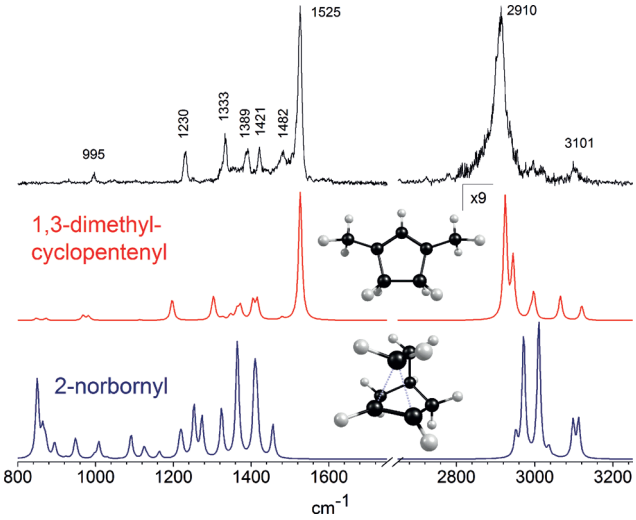

Figure 1. Comparison of the experimental infrared spectrum of $C_7H_{11}^+$ (black, top) with spectra predicted for isomers **A** (red, middle) and **F** (blue, bottom). Calculations were performed at the MP2/cc-pVTZ level of theory. Harmonic frequencies were scaled by a factor of 0.956.

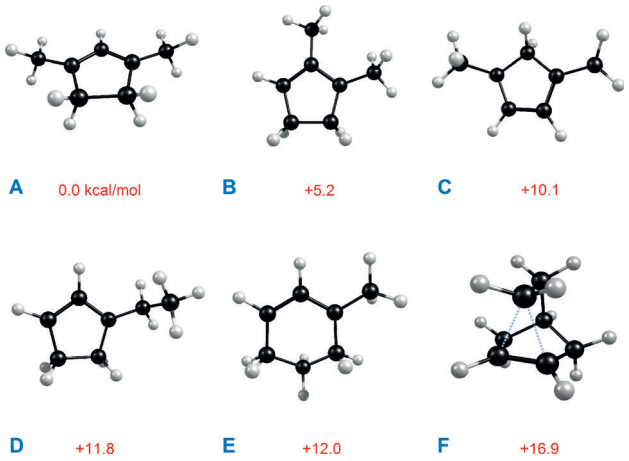

Figure 2. Six low-energy isomers of $C_7H_{11}^+$. Energies are computed at the MP2/cc-pVTZ level of theory.

does not match spectra measured for $2NB^+$ in superacid films.[13,22] In particular, $2NB^+$ has no 1525 cm^{-1} feature and its strong bands in the 1300–1400 cm^{-1} region and that near 850 cm^{-1} are not detected. These surprising results prompted a study of $2NB^+$ with different levels of theory. Computations at the DFT/B3LYP and CCSD(T) levels produce frequencies in essential agreement with those in Figure 1 (see Supporting Information). We therefore conclude that the spectrum obtained is not that of the $2NB^+$ cation.

To identify the ion produced we performed the first systematic computational investigation of $C_7H_{11}^+$ isomers.[20,28,29] 10 isomers were identified (see Supporting Information); the six lowest of these appear in Figure 2. Isomers **A**, **E** and **F** were investigated further at the CCSD(T)/ANO0 level (Table 1). Corresponding MP2 and CCSD(T) energies are comparable, except for the $2NB^+$ structure, where MP2 overestimates the stability indicated by CCSD(T). As shown in these data, $2NB^+$ is far from the most stable structure for $C_7H_{11}^+$. Instead, the 1,3-dimethylcyclopentenyl cation ($DMCP^+$) is the global energy minimum, lying 23.4 and 16.9 kcal mol^{-1} lower than $2NB^+$ at the CCSD(T) and MP2 levels. Merino and co-workers have carried out a complimentary molecular dynamics study of the $2NB^+$ potential energy surface and its rearrangement pathways, also finding $DMCP^+$ as the global minimum.[31] When vibrational spectra for these isomers are examined (see Supporting Information), only that for the $DMCP^+$ species (Figure 1, middle) matches the experiment. The main experimental features are all accounted for, and no strong bands are predicted that are not observed. Apparently, our experiment produces the $DMCP^+$ isomer exclusively.

Previous gas-phase studies of $2NB^+$ also employed protonation of norbornene to produce this ion.[23–27] However, the ions formed in our experiment rearranged to form the $DMCP^+$ species. The energetics of the protonation provide some insight into this rearrangement. Because H_3^+ (convenient for our discharge source) has a proton affinity (100.9 kcal mol^{-1})[32] much lower than that of norbornene (198.8 kcal mol^{-1}),[26] the reaction is exothermic by almost 100 kcal mol^{-1}. According to the molecular dynamics study of Merino,[31] ring-opening steps for $2NB^+$ require activation energies near 30 kcal mol^{-1}. It is therefore not too surprising in retrospect that our protonation could cause rearrangement of $2NB^+$. However, our ion source employs a supersonic expansion in which collisional cooling occurs within a few microseconds to temperatures of 50–100 K. Therefore, although the protonation was exothermic, rearrangement was not guaranteed. Previous gas-phase studies of $2NB^+$ employed less exothermic norbornene protonation or generated ions from norbornyl halide precursors.[23–27] Unfortunately, such reagents are intractable thusfar in our discharge source, preventing the formation of $C_7H_{11}^+$ by those routes. However, although the previous studies employed less energetic ionization, they used no collisional cooling. Ion fragmentation was observed, suggesting that isomerization could also have influenced those studies.

The $DMCP^+$ cation, seen here for the first time in the gas phase, is fascinating in its own right. It has been characterized before only as an ion pair in zeolite matrices by

Table 1: Structural isomers of $C_7H_{11}^+$ predicted on the 0 K potential energy surface.[a]

Isomer	MP2/cc-pVTZ [hartree]	ΔE [kcal mol^{-1}]	CCSD(T)/ANO0 [hartree]	ΔE [kcal mol^{-1}]
1,3-dimethylcyclopentenyl (**A**)	−272.4691985	0.0	−272.4017756	0.0
1,2-dimethylcyclopentenyl (**B**)	−272.4608720	+5.2	–	–
1,4-dimethylcyclopentenyl (**C**)	−272.4538149	+10.1	–	–
1-ethylcyclopentenyl (**D**)	−272.4521393	+11.8	–	–
1-methylcyclohexenyl (**E**)	−272.4522731	+12.0	−272.3862355	+11.0
2-norbornyl (**F**)	−272.4469651	+16.9	−272.3689254	+23.4

[a] Structures optimized at the MP2/cc-pVTZ level of theory were confirmed to be minima through harmonic vibrational analysis. Selected isomers were evaluated at the CCSD(T)/ANO0 level.

Table 2: Vibrational bands for the 1,3-dimethylcyclopentenyl (C_{2v} symmetry) cation compared to the predictions of theory and previous Raman experiments.[a]

Exp.[b]	MP2[c]	CCSD(T)[d]	Raman[e]	Symmetry	Assignment[f]
995	977 (22.6)	987 (81.9)	1000	b_1	ip CH_3 δ_{asym}/CH_2 twist/CH out-of-plane wag
1230	1197 (67.6)	1219 (707.9)		b_2	ip CH_2/CH wag
1333	1300 (18.1)	1322 (48.7)		a_1	ip C_2 (ring) stretch, ip CH_3 umbrella
	1304 (68.2)	1324 (156.2)		b_2	oop C_2 (ring) stretch, ip CH_2 wag
1389	1363 (35.7)	1381 (5.6)	1375	b_2	oop CH_2 scissors, asym ring distortion
	1372 (51.8)	1392 (68.8)		a_1	ip CH_2 scissors
1421	1404 (60.7)	1435 (25.2)	1440	b_1	ip CH_3 asym bend
	1418 (45.5)	1425 (20.8)		b_2	oop CH_3 asym bend/CH in-plane wag
1482	1479 (9.5)	1456 (1.2)		a_1	C_3 (allyl) sym stretch
1525	1528 (446.8)	1514 (223.8)		b_2	C_3 (allyl) asym stretch
2910	2923 (41.9)	2890 (25.0)		b_2	oop CH_3 sym stretch
	2945 (19.5)	2929 (12.5)		a_1	ip CH_2 sym stretch
2995					
3017	3065 (8.8)	3034 (10.3)		b_2	oop CH_3 in-plane C–H stretch
3101	3119 (4.7)	3121 (783.9)		a_1	allyl C–H stretch

[a] Frequencies are in cm^{-1}; intensities in parentheses are in $km\,mol^{-1}$. [b] This work. [c] Frequencies of $C_7H_{11}^+Ar$ scaled by a factor of 0.956; basis sets were cc-pVTZ for C and H atoms, aug-cc-pVDZ for Ar atoms. [d] Anharmonic frequencies for $C_7H_{11}^+$ from harmonic frequencies computed at the CCSD(T) level using a truncated atomic natural orbital basis set (ANO0) and anharmonic corrections obtained at the MP2/ANO0 level coupled with second-order vibrational perturbation theory (VPT2). [e] From Ref. [34]. [f] ip = in phase; oop = out of phase.

^{13}C NMR[33] and low-resolution Raman spectroscopy.[34] Its structure combines carbocation-stabilizing features: five-membered ring allyl resonance and optimally-placed methyl substituents. The intense C-C-C asymmetric allyl stretch at 1525 cm^{-1} is lower than the corresponding vibrations of the allyl cation (1581 cm^{-1})[35] or protonated benzene (1607 cm^{-1}).[36] The prominent 2910 cm^{-1} absorption corresponds to the overlapping C–H stretches of the CH_3 and CH_2 groups. Lower frequency bands arise from C–H bending and carbon stretching modes. As shown in Table 2, some Raman bands from zeolites correspond approximately with our gas-phase IR bands.[34] Therefore, the assignment of the $C_7H_{11}^+$ ion in our experiment to $DMCP^+$, the $C_7H_{11}^+$ global minimum, is unambiguous.

It is clear from this work that the global potential energy surface of the $C_7H_{11}^+$ ion connecting to $2NB^+$ is complex, with a rich variety of structures and rearrangement pathways not recognized previously. Merino's related study[31] finds that several structures other than $DMCP^+$ lying lower in energy than $2NB^+$ are highly relevant in the mechanistic dynamics on this PES. Rearrangements of related bicyclic ions have been studied previously, and found to proceed through cyclohexenyl intermediates before forming cyclopentenyl species related to $DMCP^+$.[37] Considering the possible isomer intermediates and rearrangement pathways, it is truly remarkable that we produced only the $DMCP^+$ ion. This study provides the first spectroscopy of any $C_7H_{11}^+$ ion in the gas phase, without the stabilizing influences of counter ions or solvent. Previous gas-phase experiments also employed energetic ionization, but without collisional cooling, and may also have been subject to facile rearrangements. It therefore remains to be seen whether or not the authentic $2NB^+$ cation has been or can be produced as an isolated ion in the gas phase.

Experimental Section

$C_7H_{11}^+$ ions are produced in a pulsed discharge source[30] and cooled in a supersonic expansion using a gas mixture of 10% H_2 in argon (total pressure 20 atm) seeded with the vapor of norbornene (Sigma–Aldrich) heated to 40 °C. The molecular beam is sampled into a reflectron time-of-flight mass spectrometer in a differentially-pumped chamber. $C_7H_{11}^+$ tagged with argon or N_2 (m/z 135/123) is mass-selected and irradiated with a tunable IR laser (LaserVision OPO/OPA).[30] Parent and fragment ions are then detected at different times with an electron multiplier tube. IR spectra are recorded as the $C_7H_{11}^+$ signal resulting from argon elimination while tuning the laser. MP2 calculations employed the GAMESS-US package (v. 1 May 2012, R1).[38] CCSD(T) calculations were carried out with the CFOUR program (version 1.0).[39]

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