

Route to a Kinetically Stabilized Protonated Spirocyclopentane with a Pentacoordinated Carbon Atom. The Missing Link between Bicyclo[3.2.0]hept-3-yl and 7-Norbornyl Cation

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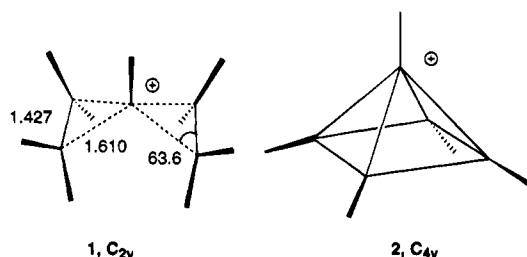
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The structure of center-protonated spirocyclopentane (1) has intrigued both theoreticians and experimentalists.^{1–4} The most peculiar feature of this cation is a pentacoordinated pyramidal carbon atom.^{3,4} In this respect, 1 is closely related to protonated pyrimidine (2) and its derivatives that were the first experimentally investigated cations with a pentacoordinated carbon atom (Chart 1).^{5–7} However, the angle strain imposed by the planar cyclobutyl moiety considerably destabilizes 2, while such a strain is absent in 1. Since kinetic and thermal instability of strained systems such as 2 represent major difficulties for synthesis and spectroscopic investigation,⁸ 1 might serve as a much better model compound for detailed studies on the physical properties of carbocations with a pyramidal pentacoordinated carbon atom.

Gas-phase studies by Cecchi and co-workers⁴ and condensed phase studies by Franke and co-workers³ provided *indirect* evidence for the existence of 1. However, isolation and direct investigation of 1 is severely hampered by its low kinetic stability resulting from a facile isomerization to the cyclopentyl cation (activation barrier: 6 kcal/mol).⁴ In this paper, we describe an ethano-bridged derivative of the center-protonated spirocyclopentyl cation, namely the tricyclo[4.1.0.0^{1,3}]heptyl cation 3, that is remarkably stabilized compared to its parent compound. The ethano-bridge does not affect the pyramidal geometry and the state of coordination of carbon atom C3 but considerably increases the activation energy of a rearrangement to cyclopentyl derivatives.

Computational Methods. The potential energy surface (PES) of C₇H₁₁⁺ has been explored in the vicinity of the tricyclo[4.1.0.0^{1,3}]heptyl cation 3 and related carbocation structures 4–7 (Figure 1) at the Hartree–Fock (HF) and the second-order Møller–Plesset (MP2) perturbation level of theory employing the 6-31G(d) basis set. Harmonic frequencies have been calculated in all cases at the HF/6-31G(d) level and, in selected cases, also at the MP2/6-31G(d) level in order to characterize calculated stationary points and to determine zero-point energies

Chart 1



(ZPE) as well as other vibrational corrections. Single point calculations with MP2/6-31G(d) geometries have been carried out at fourth-order MP (MP4) theory including single (S), double (D), and quadruple (Q) excitations (MP4(SDQ)).

NMR chemical shift calculations have been performed with the IGLO (individual gauge for localized orbitals) method of Kutzelnigg and Schindler^{9–11} in a version designed for routine calculations within the programs COLOGNE94¹² and GAUSSIAN92.¹³ The (9s5p1d/5s1p) [5s4p1d/3s1p] basis set recommended by Kutzelnigg and co-workers¹¹ for ¹³C NMR calculations was employed.

Geometry and Conformation of 3. MP2 geometry optimization of the tricyclo[4.1.0.0^{1,3}]heptyl cation leads to the C₁-symmetrical form 3a. Calculation of MP2 vibrational frequencies reveals that 3a is a local minimum on the C₇H₁₁⁺ PES. The CC bonds lengths at the pentacoordinated carbon atom C3 are in the range of 1.57–1.65 Å (Table 1, Figure 2), which is comparable to the corresponding bond lengths (1.61 Å⁴) in 1. Distance C1C5 (2.43 Å) is significantly shorter than C1C5 (2.6 Å) in 1 as a consequence of geometrical constraints imposed by the ethano-bridge.

The pyramidal configuration of the pentacoordinated atom C3 in 3a resembles that of the corresponding C atom in 1. Atoms C1C2C4C5 are in the same hemisphere in an almost planar rectangular arrangement ($\tau_{1245} = 13^\circ$), while the apical atom H3 is in the other hemisphere with the C3H3 bond being perpendicular to the plane of the basal C atoms. Form 3a can easily rearrange ($\Delta E^\ddagger = 1.9$ kcal/mol, MP4(SDQ)/6-31G(d)+ZPE) to its enantiomer 3c passing through a C_s-symmetrical transition structure 3b (Figure 1). Obviously, twisting of the ethano-bridge of 3a leads to partial strain relief and the energy difference of 1.9 kcal/mol between 3a and 3b.

Kinetic and Thermodynamic Stability of 3. Cation 3a can rearrange to the cyclopentyl cation derivatives 5 and 7 (Figure 1), namely the bicyclohept[3.2.0]-3-yl cation 5 and the 7-norbornyl cation 7. In the course of the rearrangement 3a → 5 distance C1C5 is shortened, while distances C1C3 and C5C3 are considerably lengthened. The rearrangement proceeds via TS 4 (C1C3 = 2.21 Å, C3C5 = 2.28 Å, C1C5 = 1.57 Å, Table 1) surmounting an activation barrier of 18.9 kcal/mol (MP4(SDQ) + ZPE, Table 1 and Figure 1) that is considerably

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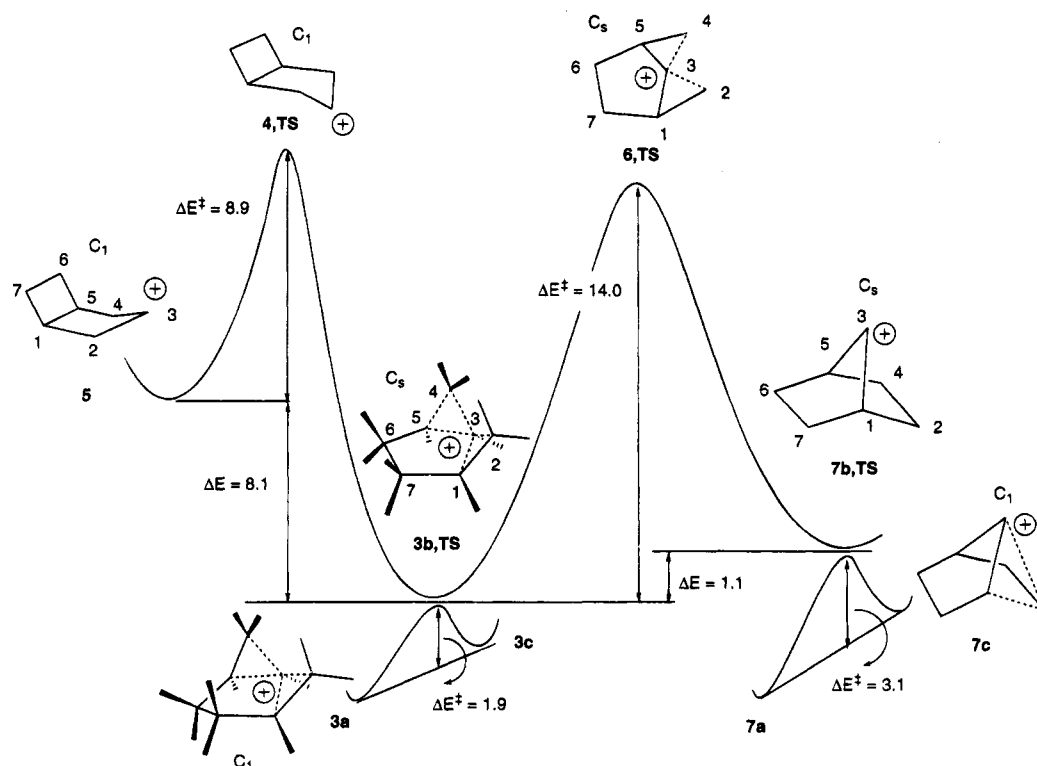


Figure 1. Potential energy surface of $C_7H_{11}^+$ in the region of cation structures 3–7 according to MP4(SDQ)/6-31G(d)/MP2/6-31G(d) + ZPE calculations. All energies in kcal/mol. Carbon atoms are numbered uniformly according to the numbering in cation 5.

Table 1. MP2/6-31G(d) Geometries and MP4(SDQ)/6-31G(d)/MP2/6-31G(d) Energies of Molecules 3–7^a

parameter	3a C_1	3b C_s	4 C_1	5 C_1	6 C_s	7a ^b C_1	7b ^b C_s
C1C2	1.428	1.432	1.600	1.526	1.491	1.886	1.595
C1C3	1.622	1.628	2.208	2.365	1.477	1.388	1.443
C1C5	2.432	2.433	1.569	1.556	2.450	2.636	2.337
C2C3	1.617	1.594	1.433	1.440	1.787	1.778	2.033
C2C4	2.636	2.617	2.461	2.399	2.018	1.550	1.584
C3C4	1.568	1.594	1.471	1.441	1.787	2.180	2.033
C4C5	1.437	1.432	1.547	1.537	1.491	1.537	1.595
C5C6	1.512	1.520	1.550	1.543	1.532	1.534	1.533
C6C7	1.528	1.543	1.547	1.547	1.563	1.549	1.559
C1C2C3	64.0	64.8	92.2	105.8	53.1	44.4	44.9
C2C3C4	111.6	110.3	115.8	112.8	68.8	44.7	45.9
C3C4C5	66.7	64.8	98.1	107.6	53.1	44.4	44.9
C4C5C6	123.7	121.5	119.7	114.6	114.9	113.0	109.4
C5C6C7	104.7	107.0	89.1	89.1	106.9	105.6	104.7
C6C7C1	103.9	107.0	89.2	88.6	106.9	103.8	104.7
C1C7C6C5	33.8	0	17.0	17.2	0	17.9	0
imag freq	0	1 ^c	1 ^c	0 ^c	1	1	0
ZPE ^c	96.0	95.9	94.1	94.5	95.5	96.1	96.0
energy ^d	-272.165 94	-272.162 81	-272.132 75	-272.147 59	-272.139 80	-272.166 20	-272.161 22
rel energy + ZPE corrn	0	1.9	18.9	10.0	15.9	-0.1	3.0

^a Distances in Å, angles in deg, ZPE in kcal/mol, absolute energies in hartree, and relative energies in kcal/mol. Imag freq denotes the number of imaginary frequencies calculated at the MP2/6-31G(d) level of theory. ^b Taken from ref 14. ^c Calculated at the HF/6-31G(d) level. MP2/6-31G(d) ZPE values are as follows: **3a**, 97.0; **6**, 96.3 kcal/mol. The scale factors used at the HF and MP2 levels are 0.87 and 0.92, respectively.

higher than the activation barrier (6 kcal/mol) of the corresponding rearrangement of **1**. Cation **5** is 10 kcal/mol less stable than the spirocyclopentyl derivative **3**, which has to be compared with a ΔE of -13 kcal/mol in the case of **1** and the cyclopentyl cation.⁴ A major part of the destabilization of cation **5** is due to the strain in the four-membered ring moiety C1C5C6C7, which should be at least 27 kcal/mol.

A decrease of the distance C2C4 in **3a** and a concomitant lengthening of distances C2C3 and C3C4 leads to the formation of the 7-norbornyl cation **7a** or its enantiomer **7c**. On the route to **7**, the C_s -symmetrical TS **6**

(C2C3 = 1.79 Å, C2C4 = 2.02 Å, Table 1) is passed, the energy of which represents a barrier of 15.9 kcal/mol (Table 1, Figure 1). Hence, the two possible rearrangements of cation **3a** to a cyclopentyl cation derivative both have much higher barriers than the opening of **1** to the cyclopentyl cation. Accordingly, it is justified to speak in the case of **3a** of a kinetically stabilized center-protonated spirocyclopentyl cation.

Recent matrix isolation studies and ab initio investigations have focused on the 7-norbornyl cation **7**.^{14,15} The C_s -symmetrical form **7b** is the TS of the "same-side bridge flipping" process.¹⁴ It is interesting to note that rear-

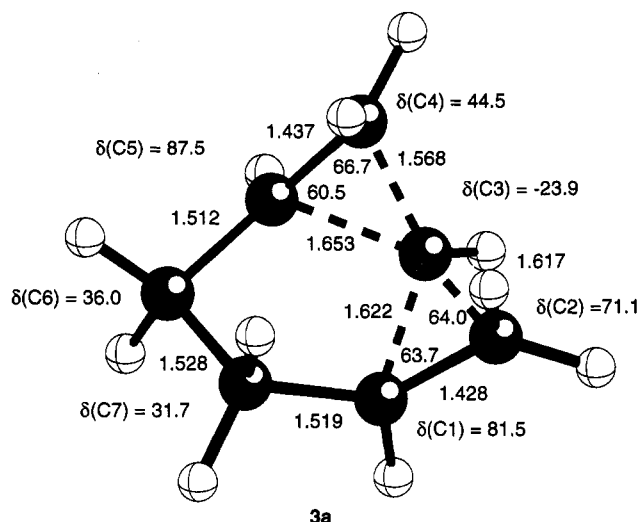


Figure 2. MP2/6-31G(d) geometry (bond lengths in Å and angles in deg) and IGLO/[5s4p1d/3s1p] ^{13}C chemical shifts (in ppm relative to TMS) of cation **3a**.

rearrangement of **3a** to **7a** proceeds via three consecutive TSs **3b**, **6**, and **7b** without any intermediate. When going from **5** to **7a** even four consecutive TSs, **4**, **3b**, **6**, **7b**, without any intermediate are passed. This has been confirmed by intrinsic reaction coordinate calculations and will become understandable if one considers that **3b** and **7b** are TSs for racemization, the reaction paths of which are perpendicular to the rearrangement path **5** $\rightarrow$ **7**. A similar situation has recently been found for the degenerate rearrangements of the barbaralyl cation and has been called a double bifurcation mechanism.¹⁶ Double bifurcation mechanisms seem to occur in the rearrangements of polycyclic carbocations and are an important indicator of structural flexibility. In the present case, the bifurcation mechanism connects the domains of the bicyclo[3.2.0]hept-3-yl cation **5** and the 7-norbornyl cation **7** on the $\text{C}_7\text{H}_{11}^+$ PES via the ethano-bridged cation **3**. Hence, cation **3** is the *missing link* between the two carbocations **5** and **7**, which have attracted a lot of interest among organic chemists. Cation **3** can also be considered as the first bishomoallyl cation that is not stabilized by homoaromatic electron delocalization. Because of its relatively high kinetic stability, **3a** can probably be generated and observed by spectroscopic methods. To facilitate detection of **3a** by NMR spectroscopy, we will discuss in the following its ^{13}C NMR chemical shifts.

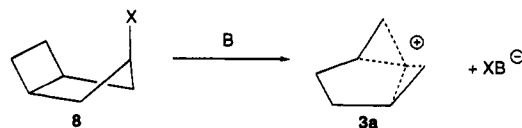
^{13}C NMR Chemical Shifts. IGLO/[5s4p1d/3s1p] ^{13}C chemical shifts calculated for **3a** are given in Figure 2.

The most characteristic shift value is that of the pentacoordinated C atom C3 which is calculated to be -23.9 ppm.^{8,11,17} None of the other known carbocations on the $\text{C}_7\text{H}_{11}^+$ PES possesses a similar shift value which means that **3a** can be unambiguously identified by its ^{13}C NMR spectrum.

A ^{13}C NMR shift value more than 20 ppm upfield relative to TMS might be unexpected for a cationic center. However, Kutzelnigg and co-workers^{11,17} have shown that carbonium ions with pentacoordinated carbon do not show the strong deshielding of carbenium ions with tricoordinated carbon (e.g., CR_3^+). Deshielding of C^+ observed for the latter results from paramagnetic currents in the plane of the σ -bonds, which depend on the availability and energy of an empty $p\pi$ -orbital since they are caused by σ - π excitations. In the way, the $p\pi$ -orbital is filled because of pentacoordination such as in **3a**, paramagnetic deshielding contributions to the ^{13}C shift value vanish, and small diamagnetic shielding contributions dominate the ^{13}C shift value.

A Synthetic Route to Formation of Cation 3a. Formation of protonated pyramidanones (**2**) is preparatively demanding⁸ since it involves synthesis and rearrangement of very strained and unstable homotetrahedran (tricyclopentane) precursors.⁵⁻⁷ So far, the parent compound **2** has not been prepared because alkyl substituents are needed to increase the thermodynamic and kinetic stability of **2**.⁵⁻⁷

Contrary to **2**, cation **3a** should be easily formed by ionization of **8**.



However, formation of the kinetically unstable cation **5** has to be avoided. This could be achieved by choosing the right leaving group X, optimizing reaction conditions, and exploiting anchimeric assistance of the cyclobutyl ring in the dissociation process. A similar strategy has successfully been applied for the generation of trishomocyclopropenium cations from 3-bicyclo[3.1.0]hexane derivatives.^{18,19}

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