Structures of Protonated Cubane

Protonation of Cubane in the Gas Phase: A High-Level Ab Initio and DFT Study**

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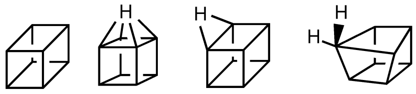
We are presently studying ion–molecule reactions of some cubane[1] derivatives. This prompted us to examine the protonation of the parent compound **1**, for which Fourier transform ion cyclotron resonance (FT-ICR) spectroscopy studies[2] led to experimental gas-phase basicities GB(**1**) of 200.7 ± 3.0[2] and 199.2 ± 3.0 kcal mol^{-1}.[3] Here we report the main results of ab initio and DFT calculations on this reaction.[4]

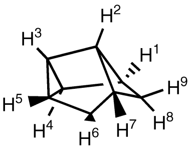
Cubane has three potential basic sites: face, edge, and corner.[5] On protonation, they lead to $\mathbf{1}H_f^+$ (C_{4v}), $\mathbf{1}H_e^+$ (C_{2v}), and $\mathbf{1}H_c^+$ (C_s; Scheme 1), respectively. The first two sites are expected to be favored by the buildup of negative charge in highly strained C–C bonds,[6] while bending of a C–H bond shifts the negative charge towards the carbon atom.[6]



1 $\mathbf{1}H_f^+$ $\mathbf{1}H_e^+$ $\mathbf{1}H_c^+$

Scheme 1. Cubane and its different protonated forms.

At the B3LYP/6-311 + G(d,p)[7] and MP2/6-311 + G(d,p) levels,[8] we find that $\mathbf{1}H_c^+$ is more stable than $\mathbf{1}H_f^+$ and $\mathbf{1}H_e^+$ by 108.7 (104.5) and 54.1 (56.7) kcal mol^{-1}, respectively (in terms of total energies; for full details, see Supporting Information). None of the three structures appears as a minimum on the potential energy surface of protonated cubane ($\mathbf{1}H^+$). The imaginary vibrational frequencies[9] in structures $\mathbf{1}H_e^+$ and $\mathbf{1}H_f^+$ are associated with the motion of the proton towards a carbon atom. Relaxation of symmetry constraints on structures $\mathbf{1}H_c^+$, $\mathbf{1}H_e^+$, and $\mathbf{1}H_f^+$ leads to the same open structure, $\mathbf{1}H_o^+$ (C_1 symmetry), corresponding to tetracyclo[4.2.0.0^{2,4}.0^{3,8}]oct-7-ylium cation (Scheme 2). This opening of the rigid framework of **1** on protonation is quite consistent with the smooth, essentially barrierless evolution of a corner-protonated structure through an electrocyclic process.[10]



$\mathbf{1}H_o^+$

Scheme 2. Tetracyclo-[4.2.0.0^{2,4}.0^{3,8}]oct-7-ylium cation.

The above results encouraged us to perform modified G2(MP2)[11] (geometries optimized and frequencies calculated at the MP2/6-311 + G(d,p) level) calculations on **1** and $\mathbf{1}H_o^+$, since we considered $\mathbf{1}H_o^+$ to be the most likely structure for $\mathbf{1}H^+$ (Table 1 and Supporting Information). The standard enthalpy and Gibbs energy changes for reaction (1), $\Delta_r H^\circ_m(1)$ and $\Delta_r G^\circ_m(1)$ thus calculated are -265.1 and -258.8 kcal mol^{-1}, respectively (Table 1).

$$\mathbf{1}(g) + H^+(g) \rightarrow \mathbf{1}H_o^+(g)\quad \Delta_r H^\circ_m(1),\ \Delta_r G^\circ_m(1) \tag{1}$$

By definition,[3] the experimental gas-phase basicity of **1**, GB(**1**), is the negative of $\Delta_r G^\circ_m(1)$. The difference between the experimental and calculated GB values thus amounts to about 60 kcal mol^{-1}. This strongly suggests that the experimental GB determined by FT-ICR spectroscopy does not correspond to the reversible protonation of **1**(g). Furthermore, the large absolute value of $\Delta_r G^\circ_m(1)$ is most consistent with the expected relief of strain attending opening of **1**(g).[2,12]

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Absolute G2(MP2) enthalpies (H_{298}, in a.u.), Gibbs energies (G_{298}, in a.u.), and corresponding relative values (ΔH_{298} and ΔG_{298}, relative to **1**, in kcal mol^{-1}) for relevant species.[a]

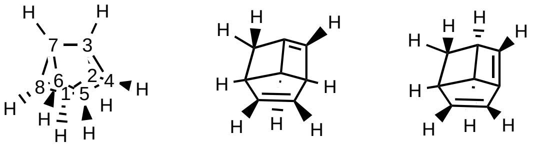
Species	H_{298}	ΔH_{298}	G_{298}	ΔG_{298}
1	−308.84989	0.0	−308.88062	0.0
$\mathbf{1}H_o^+$	−309.26858	−262.7	−309.30249	−264.7
2	−308.94420	−59.2	−308.97874	−61.6
3	−308.91972	−43.8	−308.95515	−46.8
4	−308.86704	−10.8	−308.90247	−13.7

[a] Structures fully optimized at the MP2/6-311+G(d,p) level. Numbering of species as in the text.

Reaction (2) corresponds to the protonation of **1**(g) by the acidic species BH$^+$(g) in the process taking place in the FT-ICR experiments.[2]

$$\mathbf{1}(g) + BH^+(g) \rightarrow \mathbf{1}H^+(g) + B(g) \quad \Delta_r H^\circ_m(2),\ \Delta_r G^\circ_m(2) \tag{2}$$

Since the experimental GB(B) is ca. 200 kcal mol^{-1} and the computed GB(**1**), $\Delta_r G^\circ_m(3)$, is close to 260 kcal mol^{-1} (assuming again that $\mathbf{1}H^+(g)$ has the structure $\mathbf{1}H_o^+$), it follows that the observed reaction (2) is substantially exergonic and exothermic, and isomerization of $\mathbf{1}H_o^+$ to yield some other ion of the $C_8H_9^+$ manifold cannot be entirely ruled out. We consider, however, that no isomerization of this ion occurs and explored the outcome of its deprotonation by the reference bases used in the experiments. At the B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) levels, the less endergonic processes are those corresponding to the abstraction of H^8 (or H^9), H^3, and H^1. Proton abstraction from other positions are less favored by at least 33 kcal mol^{-1} (Supporting Information). The G2(MP2) calculations were performed on the most stable deprotonated species. The results, summarized in Table 1, show that the most stable product is the hydrocarbon cuneane[13] (**2**; Scheme 3). It originates from removal of protons H^8 or H^9 [reaction (2)]. Removal of H^1 and H^3 leads to the highly strained species **3** and **4**, respectively (Scheme 3) and is less favorable.



2 **3** **4**

Scheme 3. Deprotonation products of $\mathbf{1}H_o^+$.

Importantly, the G2(MP2)-calculated standard Gibbs energy change for reaction (3), $\Delta_r G^\circ_m(3)$, amounts to 198.0 kcal mol^{-1}, a value that agrees (within the usual limits)[9,11,14] with the reported experimental gas-phase basicity of **1**. This and the clean results of ion-selection experiments described in ref. [2] are consistent with the observation in the FT-ICR studies of the protonation process (2) with $\mathbf{1}H^+$ having the structure $\mathbf{1}H_o^+$, followed by reaction (4).

$$\mathbf{1}H_o^+(g) \rightarrow \mathbf{2}(g) + H^+ \quad \Delta_r H^\circ_m(3),\ \Delta_r G^\circ_m(3) \tag{3}$$

$$\mathbf{1}H_o^+(g) + B(g) \rightarrow \mathbf{2}(g) + BH^+ \quad \Delta_r H^\circ_m(4),\ \Delta_r G^\circ_m(4) \tag{4}$$

Thus, even though **1**(g) is able to deprotonate bases with GB ≈ 260 kcal mol^{-1}, $\mathbf{1}H_o^+(g)$ can be deprotonated by bases with GB ≈ 198 kcal mol^{-1}, and, under the experimental working conditions, $\mathbf{1}H^+(g)$ is not observed in the presence of bases with GB values significantly larger than the latter value. The possibility of gas-phase isomerization through protonation/deprotonation processes is well documented.[15] It is also known that, in solution, **1** readily isomerizes to **2** in the presence of Ag^I,[13] Pd^{II},[13] or Li^I.[16] These facts support the likelihod of the suggested mechanism.

Our results strongly suggest that the gas-phase protonation of cubane is an irreversible process leading to the formation of tetracyclo[4.2.0.0^{2,4}.0^{3,8}]oct-7-ylium cation ($\mathbf{1}H_o^+$). It is likely that under the experimental FT-ICR conditions, this process is followed by the deprotonation of this ion to yield cuneane. These conclusions are perfectly consistent with the experimental information available. At this point we are conducting experimental studies on the gas-phase protonation of cuneane.

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[4] Full computational details are given in the Supporting Information.

[5] There is also an isomer in which the proton is located at the center of the cube (O_h symmetry). At the B3LYP/6-311+G(d,p) level, this endohedral structure, $\mathbf{1}H^+_{endo}$, is 199.7 kcal mol^{-1} less stable than $\mathbf{1}H_c^+$ and is not a minimum on the potential energy surface of $\mathbf{1}H^+$ (see Supporting Information).

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