

Is the Most Stable Gas-phase Isomer of the Benzenium Cation a Face-protonated π -Complex?

Mikhail N. Glukhovtsev,^a Addy Pross,^{*a,b} Athanassios Nicolaides^c and Leo Radom^{*c}

^a School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

^b Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel

^c Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

The recent suggestion, based on gas-phase experimental data, that the most stable isomer of protonated benzene has a face-protonated π -complex structure is not supported by our detailed computations which indicate that the π -complex is a second-order saddle point on the potential energy surface, lying 199 kJ mol⁻¹ higher in energy than the well-established C_{2v} σ -protonated structure.

Protonation of benzene is an archetypal reaction for aromatic electrophilic substitution,^{1,2} that is discussed in textbooks^{3,4} and has been examined in detail in a variety of experimental⁵⁻¹¹ and theoretical¹¹⁻¹⁹ studies. NMR investigations in superacid solution,^{8,9} solid-state IR spectroscopy experiments⁵ and semi-empirical^{11,17-19} and *ab initio*¹²⁻¹⁶ molecular orbital calculations all indicate a σ -type C_{2v} benzenium cation structure **1** for protonated benzene. A C_s edge-protonated form **2** has been found to be a transition structure for intramolecular proton-migration in **1**.^{12,14,17,19} ¹³C NMR studies find the activation barrier for proton scrambling in solution^{8,9} to be approximately 30–40 kJ mol⁻¹, while previous theoretical estimates range from 4 to 86 kJ mol⁻¹.^{12,14} The few previous studies that have considered the C_{6v} face-protonated structure **3** find it to lie much higher in energy than **1** [by 360 and 419 kJ mol⁻¹ at the HF/3-21G²⁰ and MP2(full)/4-31G(d)¹⁶ levels, respectively].

In the light of these experimental and theoretical results, the recent conclusion that the face-protonated complex is probably the most stable isomer of protonated benzene in the gas-phase²¹ is quite remarkable. This conclusion was drawn on the basis of collision-induced dissociation mass spectrometry experiments on the $C_6H_7^+$ and $C_6D_6H^+$ ions and the efficiency of loss of H and H₂. The high H-loss peak in the spectrum of $C_6D_6H^+$ was interpreted as evidence that two distinguishable isomers of protonated benzene exist and that at low temperatures the more stable isomer has a structure in which the added proton is effectively isolated from the edge-bound hydrogens. The authors²¹ assigned the structure of this more stable isomer to be the face-protonated π -complex **3**. The energy difference between the π - and σ -protonated structures was estimated²¹ to be about 16 kJ mol⁻¹.

Critical inspection of the existing computational data on the face-protonated complex **3** from the viewpoint of these experimental findings and their interpretation²¹ has revealed that the previous theoretical results,^{12,16,20} while suggesting that **3** is unlikely to be a stable structure, are not completely definitive. No rigorous calculations of the nature of the stationary point for **3** have been reported to date, either at the Hartree-Fock level or at a correlated level, although it was concluded that **3** corresponds to a saddle point on the basis of a partial constrained geometry optimization at the MP2(full)/4-31G(d) level.¹⁶

In an attempt to redress the apparent discrepancies between the theoretical¹¹⁻²⁰ and recent experimental²¹ data on the $C_6H_7^+$ cation, we have undertaken calculations on the possible isomeric structures **1**–**3** using G2(MP2) theory²² and the B3-LYP variant of density functional theory.²³ We have also carried out calculations on **3** at the MP2(fc)/6-31G(d,p) level

and at the HF level with the 6-31G(d), 6-31G(d,p) and 6-31G(d,2p) basis sets. The GAUSSIAN 94 system of programs²⁴ was used.

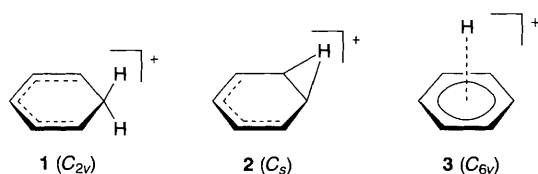
We have found that the C_{6v} π -complex structure **3** is a second-order saddle point at all the levels of theory that we have used (Table 1). The absolute values of the degenerate imaginary frequencies for **3**, are sufficiently great that it is most unlikely that this face-protonated structure could become a minimum at higher levels of theory. Polarization functions on the hydrogens tend to decrease the C–H bond lengths in **1**–**3**. However, the distance between the apical hydrogen and the ring carbons in **3** is still much longer than normal C–H bonds. Also noteworthy is the bending of the C–H bonds of the ring in **3** by 6–7° towards the apical hydrogen. It has previously been found²⁵ that the bonding between the ring and the apical group in pyramidal structures akin to **3** is optimal when there is maximum overlap without bending. In this respect, it should be noted that the bending angle for **3** is almost three times as great as the angle for the stable C_{6v} pyramidal lithium analogue (CH)₆Li⁺ (for which the bending is 2.5° away from the apical lithium).^{25,26}

In contrast to the second-order saddle-point nature of the face-protonated π -complex **3**, the C_{2v} structure **1** of the σ -protonated form (Fig. 1) is found to be a minimum, the lowest frequency (ν_1) at the B3-LYP/6-31G(d,p) level being 217 cm⁻¹. This structure is 199 kJ mol⁻¹ lower in energy than the C_{6v} structure **3** at the G2(MP2) level at 298 K.† The G2(MP2) proton affinity (PA) for benzene, obtained assuming that **1** is the most stable isomer of $C_6H_7^+$, is 747.1 kJ mol⁻¹ at 298 K, in good agreement with a recent experimental value of 753 kJ mol⁻¹.²⁷ The slightly improved result from standard G2 theory is 748.3 kJ mol⁻¹. On the other hand, the G2(MP2) PA₂₉₈(benzene) value calculated with the assumption that **3** (rather than **1**) is formed is 547.7 kJ mol⁻¹, differing significantly from all available experimental PA estimates for benzene and thus arguing strongly against such a structure. The high energy of **3** may be associated with the fact that interaction of a proton with either of the pair of highest occupied molecular orbitals of benzene is not permitted under C_{6v} symmetry. A distortion to lower symmetry (leading, for example, towards the C_s structure **1** or the C_{2v} structure **2**) is required before such interactions are symmetry allowed.§

Table 1 Selected bond lengths (Å) and harmonic vibrational frequencies (cm⁻¹) for the C_{6v} structure **3** of $C_6H_7^+$

Level of theory	<i>R</i> (CC)	<i>R</i> (CH _{basal})	<i>R</i> (CH _{apical})	ν (e ₁)
HF/6-31G(d)	1.399	1.073	1.710	2083i
HF/6-31G(d,p)	1.397	1.074	1.678	1995i
HF/6-31G(d,2p)	1.397	1.073	1.686	1943i
MP2(full)/6-31G(d)	1.409	1.086	1.690	1726i
MP2(fc)/6-31G(d,p)	1.408	1.081	1.647	1658i
B3-LYP/6-31G(d,p) ^a	1.409	1.085	1.679	1689i

^a B3-LYP/6-31G(d,p) calculations for benzene yield *R*(CC) and *R*(CH) values of 1.396 and 1.086 Å, respectively, compared with recent experimental values of 1.3902 and 1.0862 Å.²⁷ MP2(full)/TZ2P+f calculations on benzene yield *R*(CC) = 1.3896 and *R*(CH) = 1.0804 Å.²⁸



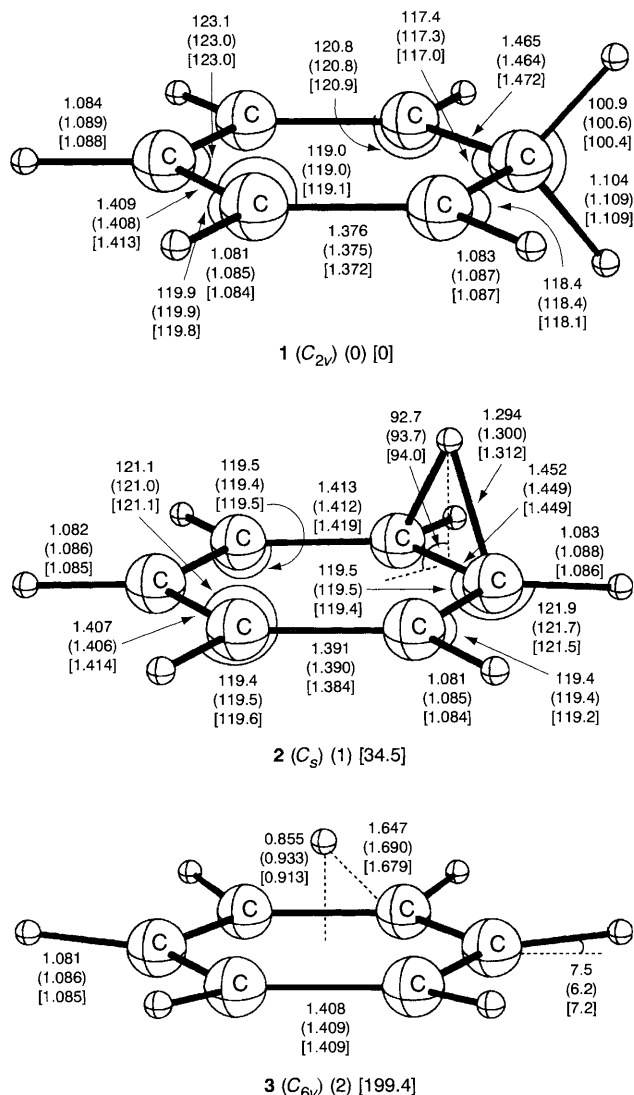


Fig. 1 Geometrical parameters of $C_6H_7^+$ structures 1–3 optimized at the MP2(fc)/6–31G(d,p), MP2(full)/6–31G(d) (in parentheses) and B3-LYP/6–31G(d,p) (in square brackets) levels. Number of imaginary frequencies and G2(MP2) relative energies (in kJ mol^{-1} at 298 K) are shown adjacent to the structure numbers in parentheses and square brackets, respectively.

The edge-protonated $C_6H_7^+$ structure **2** (Fig. 1) is found to be a transition structure for 1,2-proton migration in **1**, in agreement with earlier calculations. Proton (or deuterium ion) migration has been observed both in solution^{6,8} and in the gas-phase.³⁰ The G2(MP2) activation barrier of 34.5 kJ mol^{-1} at 298 K is close to the experimental estimate of approximately $30\text{--}40 \text{ kJ mol}^{-1}$ (albeit in solution).^{8,9}

We note in passing that the pyramidal C_{6v} structure analogous to **3** for $(SiH)_6H^+$ is a third-order saddle point at the HF/6–31G(d,p) and HF/6–31G(d,2p) levels, the imaginary frequencies [$\nu(e_1)$ and $\nu(b_2)$] being $2009i$ and $110i$, and $1961i$ and $103i \text{ cm}^{-1}$, respectively.

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Footnotes

† The G2(MP2) total energies for **1**, **2** and **3** at 0 K are -232.05904 , -232.04544 and -231.98270 hartrees, respectively. The G2(MP2) total energy for **3** calculated at the MP2(fc)/6–31(d,p) geometry is -231.98237 hartrees, showing that the energetic effect of using 6–31 G(d,p) instead of 6–31 G(d) optimized geometries is relatively small.

‡ For a general discussion of orbital interactions in capped benzenes, see reference 26.

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