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$$c_{cAMP} = K_{1/2} \cdot \sqrt[n]{\frac{I_{rel}}{1 - I_{rel}}}$$

the cAMP concentration that gives half-maximal channel activation (45 μM),[9] and n is the Hill coefficient (1.8). W. Bönigk, J. Bradley, F. Sesti, F. Müller, I. Boekhoff, G. V. Ronnett, U. B. Kaupp, S. Frings, *J. Neurosci.* **1999**, *19*, 5332 – 5347.

Protonated Benzene: IR Spectrum and Structure of $C_6H_7^+$**

Nicola Solcà and Otto Dopfer*

The protonation of aromatic molecules is a central process to organic chemistry. For example, protonated aromatic molecules (AH^+) occur as intermediates in electrophilic aromatic substitution reactions, probably the most characteristic reaction mechanism for aromatic molecules.[1] Spectroscopic studies in solution reveal that fundamental properties of these ion–molecule reactions depend strongly on the environment.[1,2] To separate solvation effects from intrinsic molecular properties, gas-phase studies are required.[3] However, to date, nearly all data about gas-phase protonation processes have come from mass spectrometric methods,[3] which provide only indirect and often inconclusive structural information. Spectroscopic data for direct and unambiguous structural characterization have not been reported for any isolated AH^+ ion, mainly because of the difficulties encountered in producing a large abundance of these species. Gas-phase spectra of AH^+ are desirable, not only to investigate fundamental reaction mechanisms, but also to identify these ions in terrestrial and extraterrestrial hydrocarbon plasmas, such as combustion flames[4] and interstellar media.[5]

Protonated benzene, $C_6H_7^+$, is the simplest protonated aromatic hydrocarbon and for more than half a century has served as a benchmark for investigating the mechanism of electrophilic aromatic substitutions. Most quantum chemical studies consider three binding sites for the proton to the benzene molecule (Figure 1).[6] The benzenium ion (**1**), often called the σ complex or Wheland intermediate, is the global minimum on the calculated $C_6H_7^+$ potential. The bridged structure **2** is predicted to be the lowest transition state for proton migration between equivalent σ complexes, with an activation barrier of $E_a \approx 6$–11 kcal mol^{-1}. The face-protonated π complex **3** is identified as a second-order transition state which lies ≈ 50 kcal mol^{-1} above **1**. Apart from **1**–**3**, several other less stable $C_6H_7^+$ isomers exist.[7] These isomers are not considered further, as they do not have a six-membered ring and are thus not created in the present experimental procedure.[3a,7,8]

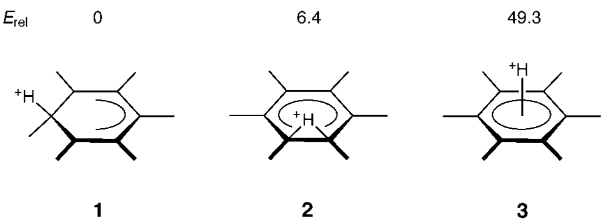

Figure 1. Calculated structures and relative energies (E_{rel} in kcal mol^{-1}) of stationary points on the potential energy surface of $C_6H_7^+$:[14] **1**: σ complex (benzenium ion, Wheland intermediate, global minimum, C_{2v} symmetry); **2**: bridged structure (benzonium ion, first-order transition state, C_s symmetry); **3**: π complex (second-order transition state, C_{6v} symmetry).

Spectroscopic evidence for a σ complex of $C_6H_7^+$ in the condensed phase comes from NMR,[9] IR,[9b,d,10] and UV spectroscopy,[10] and X-ray crystallography[9e] of either salts or superacid solutions. The low-temperature NMR spectra are consistent with a static σ complex **1**, whereas spectra recorded at higher temperatures indicate the equivalence of all protons, which is caused by rapid intramolecular exchange.[9a] The derived activation barrier for proton migration, $E_a = 10 \pm 1$ kcal mol^{-1},[9a] is consistent with the theoretical values,[6] assuming that **2** is the lowest transition state for the intramolecular 1,2-proton transfer. The conclusions drawn from gas-phase studies to ascertain the $C_6H_7^+$ structure without interference from strong solvation effects are controversial. The UV spectrum of isolated $C_6H_7^+$[11] indeed deviates significantly from the solution spectrum[10] and contains no conclusive structural information. Structure determination by mass spectrometry[3,7] suffers from indirect and disputable interpretations.[3a] Although most studies infer that **1** is the most stable $C_6H_7^+$ structure,[3a–d] a recent analysis[3e] leads to the conclusion that **3** is probably lower in energy by ≈ 3–4 kcal mol^{-1}.

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The only previous spectroscopic determination of a gas-phase AH^+ structure was recently reported for protonated phenol from IR-photodissociation spectra of its noncovalent complexes with Ar ligands.[8] The high sensitivity and selectivity of this approach overcome the problems arising from low ion concentrations.[12] The same technique is applied here to derive the vibrational spectrum and the most stable structure of protonated benzene from the spectra of weakly bound dimers with inert ligands (L). The weak interaction with L causes only a negligible perturbation of $C_6H_7^+$ and the IR spectra of $C_6H_7^+{\cdot}L$ dimers closely resemble that of the isolated ion.

Figure 2 compares the IR spectra of $C_6H_7^+{\cdot}Ar$ (a) and $C_6H_7^+{\cdot}N_2$ (b) in the vicinity of the C-H stretch vibrations. The positions, widths, and assignments of the transitions observed are collected in Table 1. The two IR spectra are almost identical, which confirms the expectation that the Ar and N_2 have essentially no influence on the IR spectrum of $C_6H_7^+$ in this frequency range.[13] Figure 2c–e shows the IR spectra calculated for the three $C_6H_7^+$ structures in Figure 1:[14] the σ complex (c), the π complex (d), and the bridged structure (e). Comparison with the theoretical IR spectra shows that the experimental spectra are clearly dominated by the σ complex **1**, because only this structure gives rise to absorptions near 2800 cm^{-1}. The two bands in the theoretical spectrum of **1** at 2823 and 2835 cm^{-1} arise from the symmetric and antisymmetric C–H stretches of the aliphatic CH_2 group (sp^3 hybridization of the C atom) and are thus an unambiguous spectroscopic fingerprint of **1**. The spectra from the experiments display three transitions in this range at ≈2795, ≈2810, and ≈2820 cm^{-1}. On the basis of their relative intensities, the first two bands are assigned to the aliphatic C–H stretching modes. Deuteration experiments discussed below show that the third and most intense band observed arises from a C–C stretch overtone ($2\sigma_{C-C}$) not included in the simulations. Two additional bands at ≈3080 and ≈3110 cm^{-1} fall in the range of the aromatic C-H stretching modes (sp^2 hybridization of the C atoms). A good agreement of relative band positions and intensities is again only observed with the spectrum calculated for **1**. Thus, the vibrational analysis demonstrates that complexes of **1** clearly dominate the measured IR spectra, whereas dimers involving **2** or **3** provide no (or at most only a minor) contribution. As the employed ion source produces predominantly the most stable AH^+ isomer, the σ complex of $C_6H_7^+$ (**1**) is concluded to be the lowest energy structure of protonated benzene, in agreement with the calculations.[6]

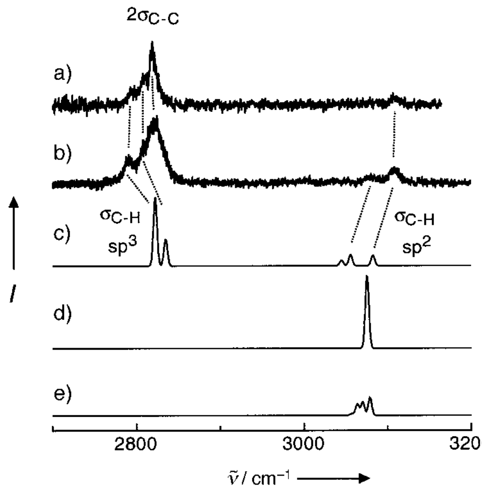

Figure 2. Experimental IR-photodissociation spectra of a) $C_6H_7^+{\cdot}Ar$ and b) $C_6H_7^+{\cdot}N_2$ in the range of the C-H stretching vibrations recorded in the $C_6H_7^+$ fragment channel. These spectra are compared to calculated spectra of three isomeric $C_6H_7^+$ structures using a convolution width of 5 cm^{-1}:[14] c) σ complex **1**; d) π complex **3**; e) bridged structure **2**. Corresponding transitions are connected by dotted lines. Aromatic C-H stretching frequencies (σ_{C-H}, sp^2) occur between 3000 and 3200 cm^{-1}, whereas bands arising from aliphatic C-H stretches (σ_{C-H}, sp^3) appear near 2800 cm^{-1}. The C–C stretch overtone ($2\sigma_{C-C}$, sp^2) is not included in the simulated spectra.

Table 1. Positions, widths (full-width half maximum in parentheses), and assignments of the transitions [cm^{-1}] observed in the IR spectra of $C_6H_{7-n}D_n^+{\cdot}Ar/N_2$ dimers.

Dimer	Position	Assignment
$C_6H_7^+{\cdot}Ar$	2795 (6)	sym σ_{C-H} (sp^3)
	2810 (8)	asym σ_{C-H} (sp^3)
	2819 (8)	$2\sigma_{C-C}$ (sp^2)
	3110 (10)	σ_{C-H} (sp^2)
$C_6H_7^+{\cdot}N_2$	2792 (9)	sym σ_{C-H} (sp^3)
	2809 (6)	asym σ_{C-H} (sp^3)
	2821 (15)	$2\sigma_{C-C}$ (sp^2)
	3081 (14)	σ_{C-H} (sp^2)
	3109 (12)	σ_{C-H} (sp^2)
$C_6H_6D^+{\cdot}N_2$	2804 (10)	σ_{C-H} (sp^3)
	2821 (16)	$2\sigma_{C-C}$ (sp^2)
$C_6D_6H^+{\cdot}Ar$	2797 (13)	σ_{C-H} (sp^3)

The IR spectra of (partly) deuterated $C_6H_{7-n}D_n^+$ ions complexed with Ar or N_2 confirm the assignments of the three bands near 2800 cm^{-1} (Figure 3, Table 1). Transitions assigned to aliphatic C-H stretch modes of the methylene group of the isotopologue $[C_5H_5CH_2]^+$ are marked by filled circles, whereas the $2\sigma_{C-C}$ overtone of the ring is indicated by an open circle.

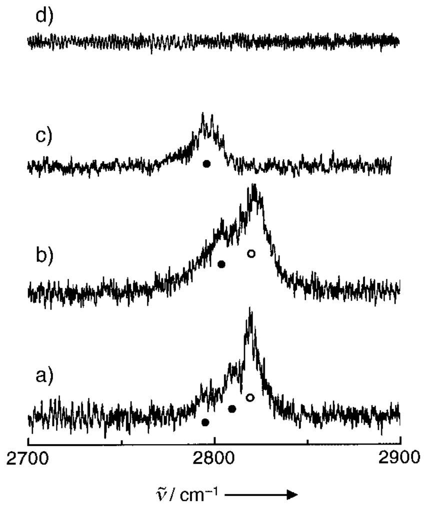

Figure 3. IR-photodissociation spectra of a) $C_6H_7^+{\cdot}Ar$, b) $C_6H_6D^+{\cdot}N_2$, c) $C_6D_6H^+{\cdot}Ar$, and d) $C_6D_7^+{\cdot}Ar$ in the range of the aliphatic C–H stretching vibrations. The intense $2\sigma_{C-C}$ overtone of the ring (open circle) is not present in the spectra c and d. The number of transitions assigned to aliphatic C-H stretches (filled circles) is the same as the number of H atoms in the methylene group.

In contrast to $C_6H_7^+$·Ar (Figure 3a), only two bands are observed for $C_6H_6D^+$·N_2 (Figure 3b), which indicates that the D atom is preferentially incorporated into the methylene group, as $[C_5H_5CHD]^+$. This cation has only one aliphatic C–H stretching mode with a frequency (2804 cm^{-1}) between the two corresponding bands of $C_6H_7^+$·Ar and $C_6H_7^+$·N_2. The intense overtone at 2821 cm^{-1} does not shift upon single deuteration of the methylene group. The $C_6D_6H^+$·Ar spectrum (Figure 3c) features a single band at 2797 cm^{-1} which is assigned to the aliphatic C–H stretch of $[C_5D_5CDH]^+$. Thus, ring deuteration shifts the overtone out of the spectral range investigated. The deuteration experiments give rise to the following main conclusions. According to Equation (1c) in the Experimental Section, single deuteronation of C_6H_6 using D_3^+ leads to the production of $[C_5H_5CHD]^+$, and similarly single protonation of C_6D_6 using H_3^+ produces only $[C_5D_5CDH]^+$. Scrambling of the transferred D/H is largely suppressed because of efficient collisional cooling down to $T < 100$ K in the ion source.[15] NMR spectra of the solution have shown that the intramolecular 1,2-proton shift in **1** is indeed suppressed at $T < 130$ K.[9a] The assignment of $2\sigma_{C\text{-}C}$ derived from the deuteration experiments is supported by our ab initio calculations and the IR spectra of the salts of the $C_6H_7^+$ isotopologues in the 1400–1600 cm^{-1} range.[9d,10] In line with the given assignments, no $C_6D_7^+$ transition is observed in Figure 3d.

The main strategy of the present work relies on the fact that the Ar and N_2 ligands have essentially no influence on $C_6H_7^+$ because of the weak interactions. Calculations confirm that this assumption is indeed valid.[14] For example, the most favorable binding site for Ar to **1** is intermolecular π bonding to the ring, with a dissociation energy of only $D_e = 1.2$ kcal mol^{-1}. Hydrogen bonds of Ar to aliphatic or aromatic protons are even less stable ($D_e < 0.8$ kcal mol^{-1}). Although the interaction of **1** with N_2 is somewhat stronger ($D_e = 2.7$ kcal mol^{-1} for the π bond), the spectra of $C_6H_7^+$·Ar and $C_6H_7^+$·N_2 are very similar. The predicted frequency shifts for the C-H stretching vibrations of **1** upon complexation with Ar or N_2[14] are significantly smaller than the widths of the observed transitions (Table 1). Hence, the perturbation of **1** by Ar or N_2 is rather minor and certainly much smaller than the solvation effects in previous condensed-phase spectra. For example, the IR spectra of $C_6H_7^+$·Ar and $C_6H_7^+$·N_2 are very different from those recorded in a salt matrix[9d] with respect to both band positions and intensities, which emphasizes the severe effects of solvation in the salt spectra.

In conclusion, the σ complex of $C_6H_7^+$ (**1**) has unambiguously been identified as the most stable structure of protonated benzene by means of IR spectroscopy, which thus solves the long-standing controversial discussion about the ground-state geometry of this fundamental ion. Interestingly, the proton differs from larger "spherical" closed-shell ions (e.g., alkali metal and ammonium ions), which prefer the formation of a π complex (cation–π interaction) rather than a σ complex.[16] The presented $C_6H_7^+$ spectrum opens the possibility for its identification in fundamental organic reaction mechanisms (e.g., aromatic substitution and proton transfer) and various hydrocarbon plasmas. The potential of the experimental approach will be used to characterize the drastic effects of stepwise solvation on the properties of ion–molecule reactions, by characterizing AH^+·L_n cluster ions as a function of cluster size (controlled solvation).

Experimental Section

IR spectra of $C_6H_7^+$·L are obtained in a tandem mass spectrometer coupled with an ion source and an octopole ion trap.[8,15] The cluster-ion source combines a pulsed molecular-beam expansion with electron-impact ionization. The expanded gas mixture is produced by bubbling either Ar/H_2/He or N_2/H_2/He buffer gas at room temperature and ≈10 bar stagnation pressure through a reservoir filled with liquid C_6H_6. For deuteration experiments, C_6D_6 and/or D_2 are used.[17] A major reaction sequence for the generation of $C_6H_7^+$·L proceeds by electron-impact ionization of H_2 [Eq. (1a)], rapid exothermic proton-transfer reactions [Eqs. (1b) and (1c)], and subsequent three-body association in the high pressure region of the supersonic expansion [Eq. (1d)]:

$$H_2 + e^- \rightarrow H_2^+ + 2\,e^- \tag{1a}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{1b}$$

$$C_6H_6 + H_3^+ \rightarrow C_6H_7^+ + H_2 \tag{1c}$$

$$C_6H_7^+ + L + M \rightarrow C_6H_7^+ \cdot L + M \;\; (L, M = C_6H_6,\ Ar,\ He,\ N_2,\ H_2) \tag{1d}$$

$C_6H_7^+$·L dimers are selected by an initial quadrupole mass spectrometer and interact in the adjacent octopole with a tunable IR laser pulse generated by an optical parametric oscillator laser system. Resonant vibrational excitation induces the cleavage of the intermolecular bond according to Equation (2):

$$C_6H_7^+ \cdot L + h\nu_{IR} \rightarrow C_6H_7^+ + L \tag{2}$$

The produced $C_6H_7^+$ fragment ions are selected by a second quadrupole mass spectrometer and monitored as a function of the laser frequency to obtain the IR action spectrum of $C_6H_7^+$·L.

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