

**FIRST AND SECOND IONIZATION ENERGIES OF  
1,3,5-TRIMETHYLBENZENE AND 2,4,6-TRIMETHYLPYRIDINE**

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The first and second ionization energies of trimethyl substituted analogs of benzene and pyridine are determined by means of mass spectrometry in conjunction with synchrotron radiation. The first ionization energy of 1,3,5-trimethylbenzene amounts to  $(8.38 \pm 0.05)$  eV and the second ionization energy to  $(22.8 \pm 0.1)$  eV. The first ionization energy of 2,4,6-trimethylpyridine is determined as  $(8.65 \pm 0.05)$  eV and the second ionization energy as  $(23.0 \pm 0.1)$  eV. The ionization energies are compared with those of unsubstituted benzene and pyridine and the effects of the methyl groups are evaluated by means of isodesmic reactions. As expected, it is found that the electron-donating effect of the methyl groups stabilizes neutral pyridine and doubly charged pyridine more than neutral benzene and doubly charged benzene, respectively. Surprisingly, the opposite effect is found for the radical cations, which is ascribed to the unfavorable degenerate electronic structure of benzene radical-cation, which disappears upon the methyl substitution.

**Keywords:** Ionization energy; Isodesmic reactions; Jahn–Teller effect; Mass spectrometry; Synchrotron; Substituent effect; Arenes.

Ionization energies belong to the most important thermodynamic characteristics of atoms and molecules. Very precise thermodynamic information can be obtained by means of zero kinetic energy photoelectron spectroscopy, which nowadays provides values of ionization energies with a precision approaching to 0.1 meV<sup>1</sup>. Electron affinities can be obtained with a very high precision up to  $\pm 0.01$  eV by photodetachment of mass-selected anions<sup>2</sup>. These methods require existence of an accessible neutral or ionic precursor.

The state-of-art mass spectrometric methods use vacuum ultraviolet (VUV) photons for the ionization of molecules. The VUV photons can be obtained from synchrotron radiation, which brings the clear advantage of smoothly tunable photon energy with a high resolution and a high photon flux in a relatively wide energetic spectrum. Ionization energies and also energetics of fragments can be derived from the threshold behavior of the corresponding ion yields in dependence of photon energy with a precision up to 5 meV<sup>3</sup>. Energetics of fragments can be also derived from the threshold behavior in collision induced dissociation<sup>4</sup>, where the precision can reach of about 50 meV. Equilibrium<sup>2,3</sup> and thermokinetic<sup>5,6</sup> experiments as well as Cook's kinetic method<sup>7,8</sup> can be named among other useful tools for the determination of the thermodynamic values of ions in the gas phase<sup>9</sup>. Last but not least, it is mandatory to mention an important role of quantum chemical methods for determination of the unknown thermodynamic properties. Some sophisticated high-level theoretical methods reach a remarkable accuracy<sup>10</sup>.

Here we aim in the determination of the first and second ionization energies of 1,3,5-trimethylbenzene and 2,4,6-trimethylpyridine using synchrotron radiation and ab initio calculations. The effect of the alkyl substitution on the ionization energies is addressed by means of isodesmic reactions. The benchmark thermodynamic values for the hydrocarbon cations and dications as well as for their nitrogen analogues are important for the derivation of relative energetics in these systems. Especially, the thermodynamics and kinetics of reactions of the hydrocarbon ions and their nitrogen analogues are important for the understanding of the chemical reactions in the planetary atmospheres and the interstellar space<sup>11-13</sup>.

## EXPERIMENTAL

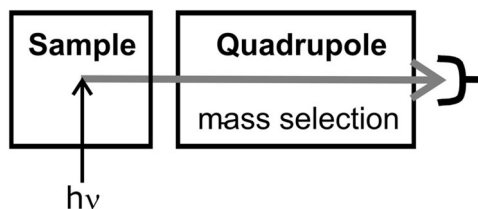
The ionization energies were measured with the CERISES apparatus<sup>14,15</sup> which was installed on the DESIRS beamline of the synchrotron radiation source SOLEIL at Saint-Aubin (France). This beamline provides monochromatic photons with energies ( $E$ ) in the range of 5–40 eV by using three different gratings. In the present experiments, the resolution was set to 10

and 50 meV in the photon energy ranges from 8 to 9 and 22 to 27 eV, respectively. For the low-energy photons, an argon filter was used in order to completely eliminate contributions from higher-order light. The photon energy was calibrated by measuring the ionization energies of helium, neon, and argon with accuracy better than  $\pm 10$  meV. Samples were introduced via a gas inlet, ionized by photons, and the so-formed ions were extracted by a field of 1 V/cm towards a QOOQ system (Q stands for quadrupole and O for octopole). The photon energy was scanned in steps of 10 meV. Q1 was used to mass-select the ions of interest, while O1, O2, and Q2 just served as ion guides.  $^{13}\text{C}$ -isotope containing dications were monitored in order to eliminate possible isobaric interferences with singly charged ions<sup>16,17</sup>. Ions were detected by a multi-channel plate operating in the counting mode. During the measurements of the ion yields, also electron yields were simultaneously recorded as well as photon fluxes, which were monitored by photoemission currents from a gold grid. The electron yields help in monitoring and hence correcting for eventual fluctuations of the pressure in the source. The raw data for the measured ion yields were corrected for the photon flux of the beam line as a function of photon energy. The contributions of background impurities to the signals of the doubly charged ions were corrected by scaling the electron yields and subtracting it from the ion yield so that the resulting corrected baseline of the photo-ion yield was zero.

The calculations were performed using the G3B3 theoretical method<sup>18</sup> implemented in the Gaussian 03 suite<sup>19</sup>, which was developed to deliver precise thermochemical values<sup>10</sup>. The structures are optimized at the B3LYP/6-31G\*<sup>20-22</sup> level of theory and the energy is further computed in a standard procedure. The energy values and thermochemistry discussed refer to a temperature of 0 K.

## RESULTS AND DISCUSSION

An apparatus for the determination of ionization energies using synchrotron radiation requires an ion source adjusted for ionization with photons (Scheme 1). The ions formed by photoionization are extracted from the source, mass-selected, and detected. The ion yield is monitored in dependence of energy of the VUV photons, and the onset of the ion yield determines the appearance energy.



SCHEME 1

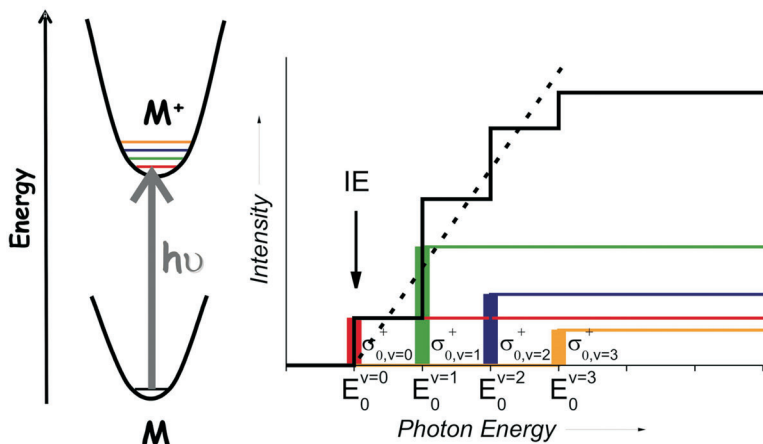
Key components of the experimental setup for the determination of appearance energies using synchrotron radiation and a mass spectrometer

The dependence of the yield of singly charged ions on the photon energy can be described by the Wannier law (Eq. (A),  $m = 0$ ,  $\sigma^+$  stands for cross section), which suggests a simple step-dependence of the ion yield on the photon energy<sup>23,24</sup>. Thus, the ion yield is zero below the ionization energy, whereas it rises as a step-function to  $\sigma_0^+$ , once the ionization energy is reached.

$$\sigma^+(E \rightarrow E_0) = \sigma_0^+(E - E_0)^m \quad (A)$$

The situation is more complicated for ionization of molecules, because many vibrational states can be populated. The ionization to each vibrational state is associated with an own ionization cross section  $\sigma_{0,v}^+$  and the observed ion yield is a sum of these individual contributions (Scheme 2). As a result, the measured ion yield usually does not resemble a step function, but rather represents a linear rise of the yield above the ionization energy. The desired appearance energy is obtained either by linear extrapolation of the onset to zero or as a first point of the rise of the ionization yield (Scheme 2).

Figure 1a shows the ion yields obtained by single ionization of 1,3,5-trimethylbenzene. The appearance energy determined from the first non-zero



SCHEME 2

Sketch of the ion-yield near threshold during photoionization of molecules to singly charged ions. The solid black line in the graph represents the idealized intensity of the generated monocations, the colored lines show the contributions of the individual vibrational states, and the dotted line depicts the determination of the ionization energy by linear extrapolation of the onset the baseline

value amounts to  $(8.34 \pm 0.05)$  eV (inset of Fig. 1a) and linear extrapolation of the onset of the ionization curve leads to a value of  $(8.38 \pm 0.05)$  eV. The first value most probably reflects the ionization of vibrationally excited neutral molecules, i.e., neutral molecules with larger internal energy are ionized to the ground state of the monocation, which leads to an appearance energy lower than the fundamental ionization energy. The value of ionization energy is therefore assigned to  $(8.38 \pm 0.05)$  eV, which is in favorable agreement with the literature value of  $(8.40 \pm 0.01)$  eV<sup>25</sup>. The

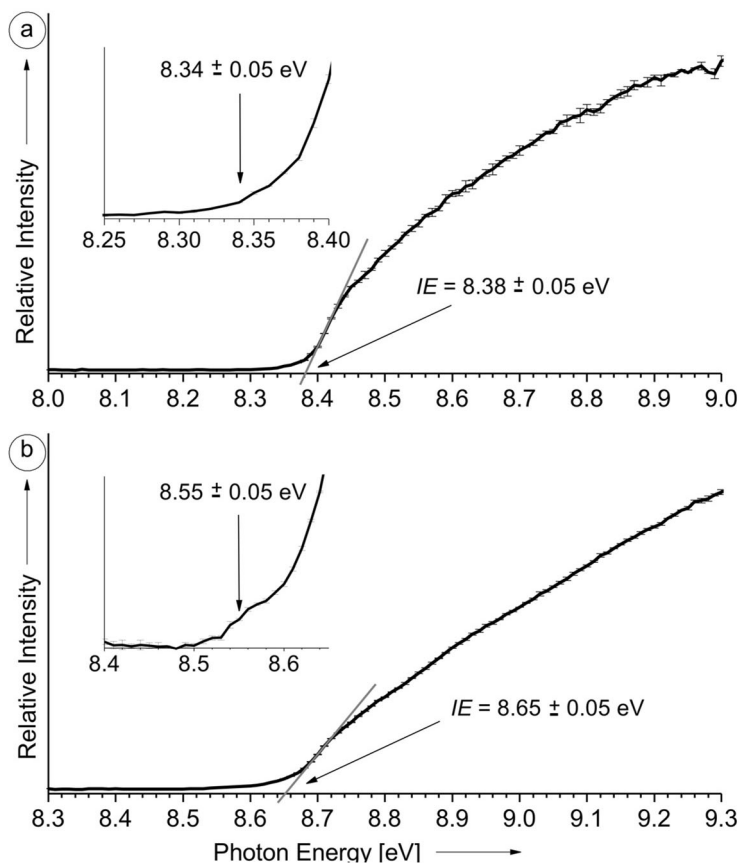


FIG. 1

Yields of molecular ions (black lines) of 1,3,5-trimethylbenzene (a) and 2,4,6-trimethylpyridine (b) in dependence of the energy of the ionizing photons. The error bars show the standard error of the mean of three independent measurements

analogous procedure for 2,4,6-trimethylpyridine leads to value of  $(8.55 \pm 0.05)$  eV as a lower limit for the appearance energy (inset of Fig. 1b) and the value of the ionization energy is again determined from linear extrapolation from the onset of the ionization curve as  $(8.65 \pm 0.05)$  eV (Fig. 1b); in the literature, only a vertical value of 8.9 eV is available for single ionization of 2,4,6-trimethylpyridine<sup>25</sup>.

The ionization energies were also obtained by means of high level theoretical calculations. The G3 method leads to values of 8.47 and 8.69 eV for the ionization energies of 1,3,5-trimethylbenzene and 2,4,6-trimethylpyridine, respectively. While, the latter value is in very good agreement with the experimental result (Table I), the former is overestimated by almost 0.1 eV. For the comparison, the same method provides values of 9.30 and 9.29 eV for the first ionization energies of benzene and pyridine, respectively, which are in reasonable agreement with the experimental values of 9.24 and 9.26 eV, respectively. Notably, however, the ionization energy of benzene is again more overestimated than that of pyridine.

Second ionization energies ( $^2IE$ ) can be also determined from the dependence of the ion yield of the corresponding dication on photon energy. The Wannier law for the second ionization cross section (Eq. (A),  $m = 1$ ) predicts that the rise of the ion yield above the ionization threshold does not represent a step function, but instead is linear (Scheme 3). The linear dependence renders the determination of second ionization energies more difficult, because the ion yield at the threshold is by definition zero and rises only slowly with energy. Both approaches used for determination of the first ionization energy fail, because the linear extrapolation leads to large errors and assignment of the first non-zero value of the ion yield is

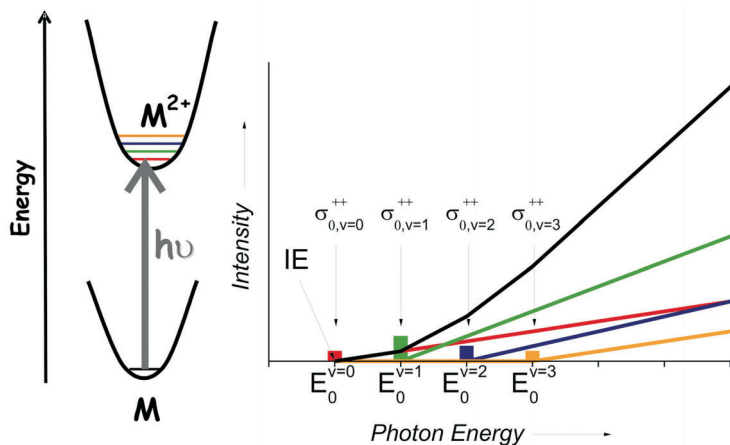
TABLE I

Experimental and calculated first and second ionization energies of benzene, pyridine, 1,3,5-trimethylbenzene, and 2,4,6-trimethylpyridine (in the calculated values for the dications, S stands for the singlet and T for the triplet states)

Compound	$^1IE_{\text{exp}}$ eV	$^1IE_{\text{calc}}$ eV	$^2IE_{\text{exp}}$ eV	$^2IE_{\text{calc,S}}$ eV	$^2IE_{\text{calc,T}}$ eV
Benzene	$9.24 \pm 0.00$ <sup>25</sup>	9.30	$24.65 \pm 0.03$ <sup>26</sup>	24.61	24.74
Pyridine	$9.26 \pm 0.01$ <sup>25</sup>	9.29	-	24.82	25.08
1,3,5-Trimethylbenzene	$8.38 \pm 0.05$	8.47	$22.8 \pm 0.1$	22.31	22.33
2,4,6-Trimethylpyridine	$8.65 \pm 0.05$	8.69	$23.0 \pm 0.1$	22.82	22.86

also vague. The state-of-art method combines the experimental data with theoretical modeling of the ionization curve, which includes calculations of Franck–Condon transition probabilities for population of excited vibrational states of dication<sup>27</sup>. Clearly, such approach is very demanding and cannot be used for large molecules. Alternatively, the curve of the ion yield can be mathematically differentiated, which – in theory – leads to a curve analogous to that obtained for single ionization<sup>12</sup>. The methods described above for the single ionization energies can be then used for the determination of the ionization energy from the differentiated curve.

The cross sections for double ionization of 1,3,5-trimethylbenzene (a) and 2,4,6-trimethylpyridine (b) are shown in Fig. 2. The values of second *IE* are determined by mathematical differentiation of the experimental curves, which were smoothed in a point averaging process in the energy interval of 0.1 eV. The appearance energy is assigned on the differentiated curve. The appearance energy of the 1,3,5-trimethylbenzene dication amounts to  $(22.8 \pm 0.1)$  eV and that of the 2,4,6-trimethylpyridine dication is  $(23.0 \pm 0.1)$  eV. The accuracy of the values of <sup>2</sup>*IE*s is lower compared to the first *IE*s, which follows from the lower abundance of the dications and less sharp onset of the corresponding ion yields.



SCHEME 3

Sketch of the ion-yield near threshold during photoionization of molecules to doubly charged ions. The solid black line in the graph represents the idealized intensity of the generated dications and the colored lines show the contributions of the individual vibrational states

In the theoretical determination of the second ionization energies it has to be considered that two low energy lying states can be populated. The G3 method suggests that the ground states of both dications correspond to the singlet states with the ionization energies of 22.31 eV for 1,3,5-trimethylbenzene and 22.82 eV for 2,4,6-trimethylpyridine. The corresponding triplet states lie only 0.02 and 0.04 eV higher in energy than the singlets. The same order of the stability of the singlet and triplet states is found also for the parent compounds benzene and pyridine (Table I). It is worth mention-

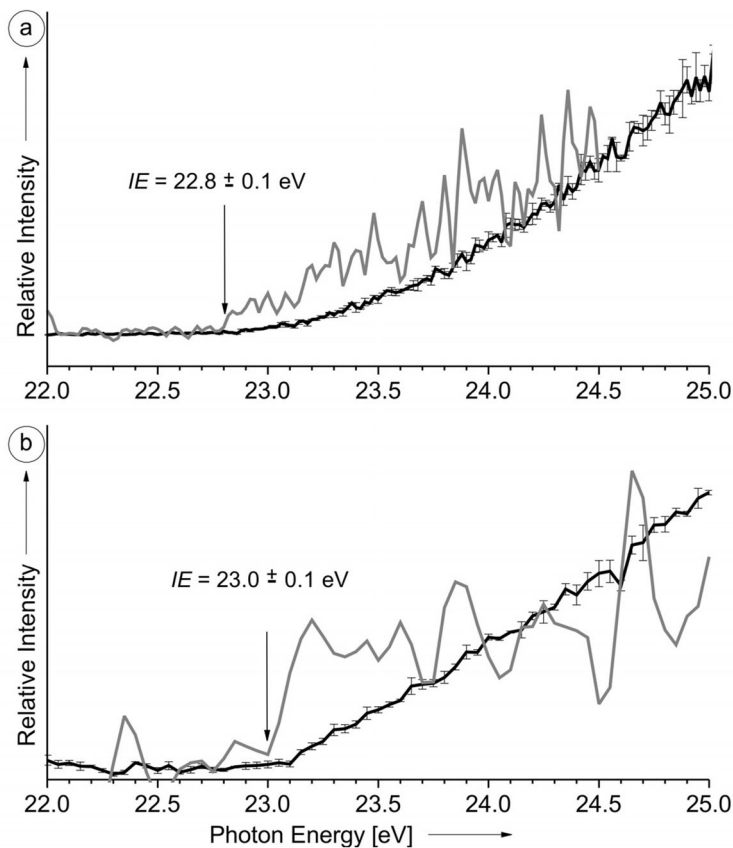


FIG. 2

Yields of molecular dications (black lines) of 1,3,5-trimethylbenzene (a) and 2,4,6-trimethylpyridine (b) in dependence of the energy of the ionizing photons. The error bars show the standard error of the mean of three independent measurements and the gray lines correspond to the derivatives of the ion yields



ing that the B3LYP method in conjunction with a triple  $\zeta$  basis set (6-311±G(2d,p)) leads to an opposite result in that the triplet states of all studied dications lie more than 0.1 eV lower in energy than the corresponding singlets.

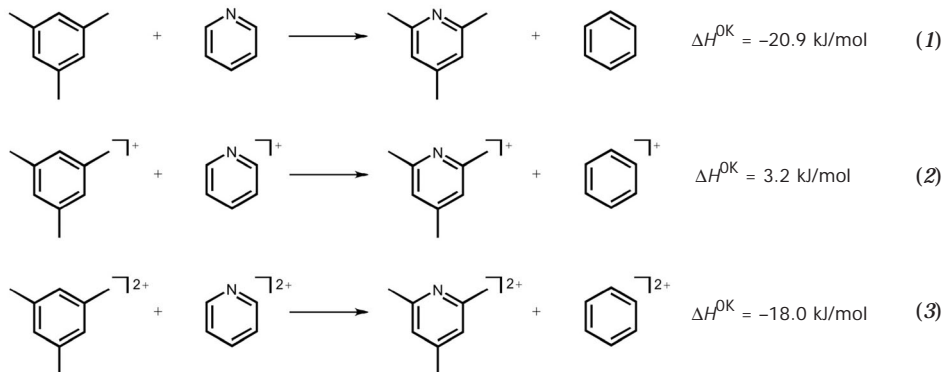
The comparison of the ionization energies obtained for 1,3,5-trimethylbenzene and 2,4,6-trimethylpyridine with the tabulated values for unsubstituted benzene and pyridine unravels several interesting findings. The ionization energies of the methyl substituted molecules are lower, which follows from the fact that larger molecules can better stabilize the charge<sup>28</sup>. The effect is about twice as big for double ionization compared to single ionization.

The effects of the presence of the nitrogen atom in the molecule are more complex. Incorporation of a nitrogen atom – a more electronegative heteroatom than carbon – to the ring leads to a slight increase of all ionization energies. The effect is surprisingly much more pronounced in the trimethyl substituted molecules, whose first ionization energies increase from 8.38 eV for 1,3,5-trimethylbenzene to 8.65 eV for the pyridine analog. In comparison, the first ionization energies of benzene and pyridine are almost equal (9.24 and 9.26 eV, respectively). This trend is in fact counter-intuitive, because it would be expected that the electron-donating methyl groups could partly compensate the electron-withdrawing effect of the nitrogen atom.

For double ionization, the experimental data cannot be compared, because the second ionization energy of pyridine is unknown. However, if we consider the calculated difference between double ionization energies of benzene and pyridine, which amounts to 0.2 eV for the singlet ground states, the effect of the methyl substitution is about the same for both molecules. The difference between the experimental double ionization energies of 1,3,5-trimethylbenzene and 2,4,6-trimethylpyridine also amounts to 0.2 eV.

The origin of the stabilization effects of methyl groups on benzene and pyridine and their singly and doubly charged states can be unraveled by means of isodesmic reactions (Scheme 4). Isodesmic reactions were developed for the accurate determination of the heats of formation of molecules by theoretical methods<sup>29</sup>, because the direct computation of heats of formation is often associated with large errors. The trick of isodesmic reactions consists in a formulation of an imaginary reaction, in which the unknown molecule is built from molecules with the known heats of formation. The equation has to be constructed so that there are the same numbers of the same types of bonds on both sides of the equation, which should lead to a

maximum cancellation of the computational error<sup>30</sup>. If for example, we would be interested in the heat of formation of 2,4,6-trimethylpyridine (TMPy) and would know heats of formation of benzene ( $\Delta_f H(\text{B})$ ), pyridine ( $\Delta_f H(\text{Py})$ ), and 1,3,5-trimethylbenzene ( $\Delta_f H(\text{TMB})$ ), we could consider the isodesmic reaction (1) and calculate its reaction enthalpy  $\Delta H_{\text{rxn,calc}}$  by a theoretical method. The heat of formation of 2,4,6-trimethylpyridine would be then simply:  $\Delta_f H(\text{TMPy}) = \Delta_f H(\text{Py}) + \Delta_f H(\text{TMB}) - \Delta_f H(\text{B}) + \Delta H_{\text{rxn,calc}}$ .



SCHEME 4

Next to this original way of using the isodesmic reactions, they can be also used to evaluate the energetic effects of various substitutions in molecules<sup>31–37</sup>. Thus, the reaction enthalpy  $\Delta H_{\text{rxn}}$  of reaction (1) expresses in fact the effect of stabilization of neutral pyridine by methyl substitution with respect to that of benzene. Similarly, Eqs (2) and (3) reveal the same effects for the radical cations and dicationic species, respectively. The reaction enthalpies were calculated using theoretical values of energies of neutral molecules calculated at 0 K and the experimental ionization energies (Table II). Here, the experimental ionization energies were used in order to eliminate the computational overestimation of the first ionization energy of 1,3,5-trimethylbenzene as well as the underestimation of its second ionization energy. The unknown experimental value for the second ionization energy of pyridine was replaced by the theoretical value.

From the results it can be concluded that for the neutral molecules pyridine experiences a larger stabilization by the introduction of three methyl groups than benzene, which is demonstrated by the fact that reaction (1) is exothermic by 20.9 kJ/mol. The opposite effect found for the radical cations in which benzene radical-cation is more stabilized by trimethylation

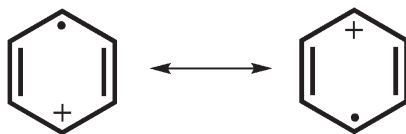
than pyridine radical-cation, i.e.  $\Delta H_{\text{rxn}}(2) = 3.2$  kJ/mol. Thus, the reason for the seemingly counterintuitive observation mentioned above consists in the larger stabilization of the benzene cation with respect to the pyridine cation upon the methyl substitution.

TABLE II

Enthalpies of benzene, pyridine, 1,3,5-trimethylbenzene, and 2,4,6-trimethylpyridine at 0 K calculated by the G3 method, the ionization energies used for the determination of theoretical enthalpies of the corresponding cations and dications, and the reaction enthalpies determined for the reactions (1)–(3)

Compound	$H_{\text{calc}}^{\text{OK}}$ , Hartree	$^1IE$ , eV	$^2IE$ , eV
Benzene	-232.057221	9.24	24.65
Pyridine	-248.098254	9.26	24.82
1,3,5-Trimethylbenzene	-349.887931	8.38	22.8
2,4,6-Trimethylpyridine	-365.936933	8.65	23.0
	$\Delta H_{\text{rxn}}(1)$	$\Delta H_{\text{rxn}}(2)$	$\Delta H_{\text{rxn}}(3)$
	-20.9 kJ/mol	3.2 kJ/mol	-18.0 kJ/mol

The origin of this effect has to be searched in the electronic structures of the radical cations. The ground state of the benzene radical-cation corresponds to a  $X^2E_{1g}$  state and is thus degenerate (Scheme 5). Substitution of the cation removes this degeneracy and leads to a Jahn-Teller splitting of the highest electronic level, which therefore leads to a second stabilizing effect of the methyl groups on the radical cation next to their mere electron-donating properties. Due to the inherently lower symmetry of pyridine, the degeneracy occurs neither in pyridine nor in its trimethyl substituted analogue and only electron-donation of the methyl groups play role. Thus, the effect of a larger stabilization of ionized benzene by methyl substitution than is the case for ionized pyridine is in fact caused by a uniquely unfavor-



SCHEME 5

Illustration of the degenerate ground state of the benzene radical-cation

able electronic structure of the unsubstituted benzene radical-cation, which disappears upon substitution.

The results for the dications (reaction (3)) are again intuitive. The methyl substitution brings a 18.0 kJ/mol larger stabilization to the pyridine dication than to the benzene dication. In agreement with the rationale drawn for the singly charged ions, there are no singularities in electronic structures found for benzene or pyridine dications and the effect revealed by the isodesmic reaction (3) just reflects the electron-donating capabilities of three methyl substituents for benzene and pyridine dications and thus follows expectation.

## CONCLUSIONS

The first and second ionization energies of 1,3,5-trimethylbenzene and 2,4,6-trimethylpyridine were determined by photoionization mass spectrometry using synchrotron radiation. The first and second ionization energies of 1,3,5-trimethylbenzene amount to  ${}^1IE = (8.38 \pm 0.05)$  eV and  ${}^2IE = (22.8 \pm 0.1)$  eV, respectively. The corresponding values for 2,4,6-trimethylpyridine are  ${}^1IE = (8.65 \pm 0.05)$  eV and  ${}^2IE = (23.0 \pm 0.1)$  eV. The effect of the methyl groups on ionization energies is unraveled using isodesmic reactions. It is found that for the neutral molecules and doubly charged ions, the stabilization by the methyl substitution is larger for pyridine than for benzene. For the radical cations, however, the stabilization is larger for benzene. The effect is ascribed to the degeneracy of the ground state of the benzene radical-cation, which is reflected in relatively high first ionization energy of benzene, which is almost equal to the first ionization energy of pyridine. In marked contrast, the second ionization energy of benzene and the first and second ionization energy of trimethyl substituted benzene are all significantly lower than values found for the corresponding pyridine. The unfavorable degeneracy of the ground state of benzene radical-cation is suspended upon substitution, which therefore leads to an additional relative stabilization of the substituted benzene radical-cation.

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