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Energetics and rearrangements of the isomeric picoline dications

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ABSTRACT

The second ionization energy of β-picoline was determined from photoionization experiments as $^{2}IE^{\beta} = (24.05 \pm 0.1)$ eV and the threshold for the dehydrogenation of the dication generated by photoionization as $AE(-H_2)^{\beta} = (25.0 \pm 0.2)$ eV. The second ionization energy is about 0.5 eV lower than values recently determined for α- and γ-picoline, whereas the energies required for dehydrogenation are similar. In order to rationalize the different behavior of dications generated from these isomeric picolines, we have performed a mass spectrometric investigation of the fragmentation patterns of the individual picoline dications and an extensive series of DFT calculations to explain the observed spectra.

1. Introduction

Double ionization of aromatic compounds often leads to rather distorted structures. In the case of benzene, for example, the removal of two electrons means that the planar aromatic π-system suddenly contains only four electrons. Thus, the benzene dication is destabilized both by the inherent Coulomb repulsion, due to the high charge density, but also electronically due to its antiaromatic configuration (in the singlet state). The geometric relaxation of the benzene dication in its singlet state, away from this destabilized geometry, favors a non-planar structure [1,2]. Double ionization can also populate triplet states of the benzene dication, the lowest lying of which is almost planar. Recent experiments have demonstrated that this triplet state is the ground state of the benzene dication [3].

Substituents often allow the stabilization of benzene dications. For example, although double ionization of toluene leads to singlet and triplet dications with geometries analogous to the corresponding states of the benzene dication [4], the presence of the methyl group allows stabilization of the dication by a variety of rearrangements [5]. The most stable dicationic structures are formed following hydrogen migrations from the methyl group to the ring carbon atoms. The resulting structures correspond to the protonated benzene molecule with positively charged exo-methylene group, i.e., the isomeric protonated benzylium ions.

Large dicationic stabilization can be achieved when two substituents are introduced to the aromatic ring, because each group can bear a charge [6,7]. Such situation is encountered for dihydroxybenzenes. In this case, in fact, double ionization transfers the molecules to the structural manifold of doubly protonated benzoquinones [8]. The relative positions of the hydroxy groups on the aromatic ring determine the stabilities of the dications which are generated. The most stable singlet dication is derived from para-dihydroxybenzene, the singlet dication derived from ortho-dihydroxybenzene lies 0.47 eV higher in energy, and the least stable singlet dication is derived from meta-dihydroxybenzene, which is 0.85 eV higher in energy than the para-derivative. While

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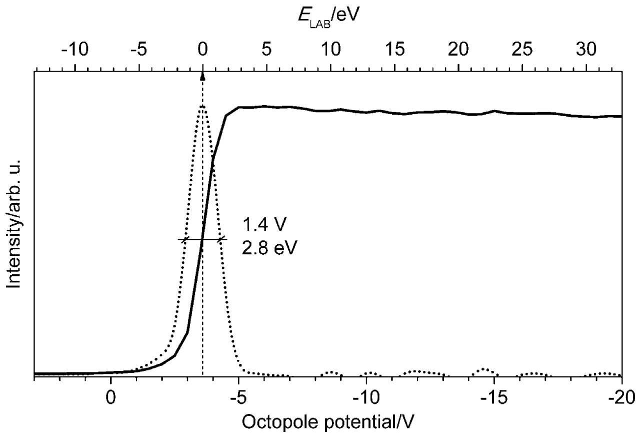


Fig. 1. Intensity of the dication beam with *m/z* 46.5 generated from β-picoline as a function of the octopole voltage. The inflexion point of the curve (the maximum of the derivative – dotted curve) is taken as the nominal zero of the laboratory-energy frame. The resulting corrected scale is on the upper axis; note that the ions are doubly charged and therefore 1 V in the potential scale corresponds to 2 eV in the kinetic energy scale.

the singlet states represent the ground states for the para- and ortho-substituted dications, the triplet and singlet states for the meta-derivative are almost isoenergetic in that the triplet state lies 0.04 eV lower in energy than singlet at the B3LYP level of theory. This energetic arrangement corresponds well with the situation for the neutral benzoquinones, where the para- and ortho-benzoquinones are stable compounds, while meta-benzoquinone is an elusive species [9,10].

In this paper we compare the stabilities of the dications derived from picolines (i.e., the isomeric methyl pyridines) [11–14]. The methyl substituent can, of course, be in a position ortho, meta, or para with respect to the nitrogen atom, leading to different electronic stabilizations of the charge and consequently access to different rearrangement pathways.

2. Experimental details

The collisional experiments were performed with a TSQ 7000 mass spectrometer equipped with an ion source for electron ionization (EI). Ionization was performed with electrons with 70 eV kinetic energy. The analyzer region of the TSQ 7000 bears a QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments [15]. The octopole, which serves as a collision cell, has a separate housing that limits the effusion of gases admitted to the octopole to the other regions of the mass spectrometer. The kinetic energy of the singly charged ions entering the octopole can be varied between 0 and 200 eV, which allows the investigation of ion/molecule reactions under quasi-thermal conditions or collision-induced dissociation (CID) at elevated kinetic energies. The ions of interest were mass-selected with the first quadrupole (Q1) at a mass resolution fully sufficient to select the corresponding dications. The mass-selected ions were then collided with xenon admitted to the octopole at a typical pressure of 10^{-4} mbar. We adjusted the collision energy by changing the offset between the first quadrupole and the octopole, whereas the offset of Q2 was locked to the sum of the offsets of Q1 and O relative to the source. The zero point of the kinetic energy scale as well as the width of the kinetic energy distribution were determined by means of retarding-potential analysis; for the dications reported here, the beam width at half-maximum was 2.8 ± 0.2 eV in the laboratory frame (Fig. 1). The nominal zero point of the kinetic energy scale was set to the point of inflection of the curve obtained by retarding potential analysis. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2 which was operated with unit mass resolution. Ion abundances were determined using a Daly-type detector operated in the analog mode. Typically, about 300 scans were accumulated per spectrum and three spectra were recorded in each experiment.

The photoionization experiments were performed with the CERISES apparatus [16–18], which was installed on the DESIRS beamline of the synchrotron radiation source SOLEIL (France) [19]. This beamline provides monochromatic photons in the range of 5–40 eV by using three different gratings. The photon energy was calibrated with an accuracy better than ± 5 meV by measuring the ionization energy of argon around 15.76 eV and the $3s3p^6np$ ($n = 5–9$) window resonances in the Ar^+ yield between 28 and 29 eV. Samples were introduced via a gas inlet and ionized by photons, and the resulting dications were extracted by a field of 1 V/cm toward a QOOQ system. The photon energy was scanned in steps of 50 meV. Q2 was used to mass-select the ions of interest, whereas Q1, O1, and Q2 just served as ion guides. Ions were detected by a multichannel plate operating in the counting mode. During the measurements of the ion yields, electron yields were also simultaneously recorded as well as the photon flux, the latter quantity was monitored via the photoemission current from a gold grid. The electron yield helps in monitoring, and hence correcting for, any fluctuations of the pressure in the source [4]. The raw data for the measured ion yields were corrected for the photon flux of the beamline as a function of photon energy.

The density functional theory calculations were performed using the B3LYP hybrid functional [20–23] together with triple ζ basis set 6-311 + G(2d,p) [24,25] as implemented in Gaussian 09 [26]. All minima and transition-state structures were verified by analysis of their Hessian matrixes. For the transition-state structures, intrinsic reaction coordinate investigations were performed, at the same level of theory, to confirm the minima they connect on the potential-energy surface [27,28].

3. Results and discussion

The double ionization energies determined from the relevant photoionization thresholds were recently published for α-picoline (2-methylpyridine) and γ-picoline (4-methylpyridine) [11]. The experimental double ionization energy of α-picoline is ${}^2IE^{\alpha} = (24.5 \pm 0.1)$ eV and that of γ-picoline is ${}^2IE^{\gamma} = (24.65 \pm 0.1)$ eV. Note, of course, that ${}^2IE(M)$ of a neutral molecule M is different from the first and second ionization energies $IE(M)$ and $IE(M^+)$; however, for the adiabatic transitions we have ${}^2IE_a(M) = IE_a(M) + IE_a(M^+)$. The dominant fragmentation channel for both dications corresponds to the elimination of H_2. The dehydrogenation thresholds were also determined in the earlier photoionization experiments with values of $AE(-H_2)^{\alpha} = (25.3 \pm 0.2)$ eV for α-picoline and to $AE(-H_2)^{\gamma} = (25.1 \pm 0.2)$ eV for γ-picoline. In order to determine the effect of meta-substitution, here we report the corresponding results (Fig. 2) obtained following double photoionization of β-picoline (3-methylpyridine).

As detailed elsewhere, an accurate determination of the adiabatic double ionization energy (${}^2IE_a$) from photodication appearance curves requires the explicit consideration of the associated Franck–Condon envelope [4,29]. Such an analysis is quite demanding however, and to date has been limited to the consideration of harmonic frequencies. Therefore, we have recently introduced a simplified method for the determination of a value for ${}^2IE$ from photoionization yield curves using an empirical fit of the dication yield (pink line in Fig. 2); Fig. 2(b) shows the deviation between the empirical fit and the experimental curve for ($\Sigma(I_i)$). Using the Wannier law for double photoionization we extrapolate the onset of the first derivative of the total dication yield ($\Sigma(I_i)$),

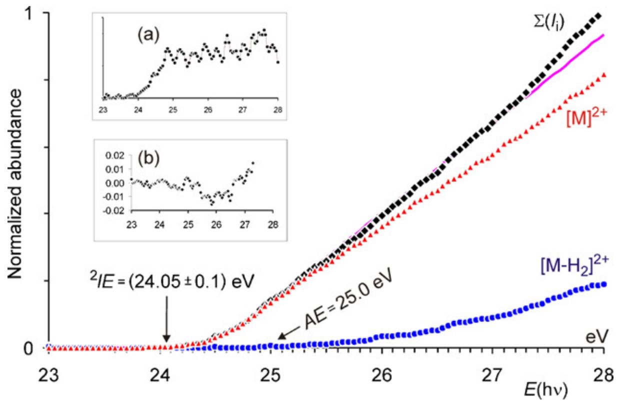


Fig. 2. Yields of the $C_6H_7N^{2+}$ dication formed upon photoionization of neutral β-picoline and of the $C_6H_5N^{2+}$ fragment formed via dissociative double ionization. Also shown is the sum of these ion yields ($\Sigma(I_i)$) as a function of the energy of the ionizing photons. Inset (a) shows the first derivative of $\Sigma(I_i)$ and inset (b) the deviation of the empirical Franck–Condon fit of $\Sigma(I_i)$ from the experimental data points.

Fig. 2(a)) to zero [30–33], which in this case leads to an experimental double ionization energy of ${}^2IE_{exp}{}^{\beta} = (24.05 \pm 0.1)$ eV. As discussed before, and below, the ${}^2IE$ value extracted from this procedure involving the first derivative of the ion yield does not necessarily correspond precisely to the adiabatic or vertical value of ${}^2IE$ [33]. The appearance energy of the $[M–H_2]^{2+}$ fragment due to dissociative double ionization is derived from the extrapolation of the linear rise to the fragment ion yield to the baseline, affording an appearance energy of $AE(-H_2)^{\beta} = (25.0 \pm 0.2)$ eV. This energy required for the elimination of H_2 is very similar to the values determined for α- and γ-picoline (25.3 and 25.1 eV, respectively [11]).

The simple comparison of the curves of the ion-yields as a function of photon energy measured for β-picoline on one hand, and for α- and γ-picoline on the other hand, reveals a significant difference. For comparison of the three isomers, the independently measured photoionization curves are normalized so that the linear rises of the curves are approximately parallel to each other; this treatment for scaling of the independently measured curve with different photoionization thresholds is based on the Wannier laws which – for ideal atoms – predict a linear rise of the ion yield above threshold for double ionization by photons [4]. While the resulting curves for α- and γ-picoline are very similar, the onset of β-picoline ionization occurs at a significantly lower photon energy (Fig. 3).

In order to rationalize the above results we have performed a series of DFT calculations. Firstly, we have calculated the adiabatic (${}^2IE_a$) and vertical (${}^2IE_v$) ionization energies for all isomeric picolines (Table 1). As in the case of benzene and toluene, the singlet and triplet states of the doubly charged picolines lie very close in energy [3,4,29]. Due to the two-fold charge, the structures of all picoline dications are distorted with respect to the neutral molecules. This distortion is reflected in relatively large differences between the calculated adiabatic and vertical energies ($\Delta{}^2IE_{v/a}$). The differences $\Delta{}^2IE_{v/a}$ are larger for the formation of singlet states of picoline dications, because their six-membered rings markedly deviate from planarity, whereas the rings stay planar in the triplet states of the picoline dications. Notably, the highest ionization energies as well as the differences $\Delta{}^2IE_{v/a}$ are determined for γ-picoline.

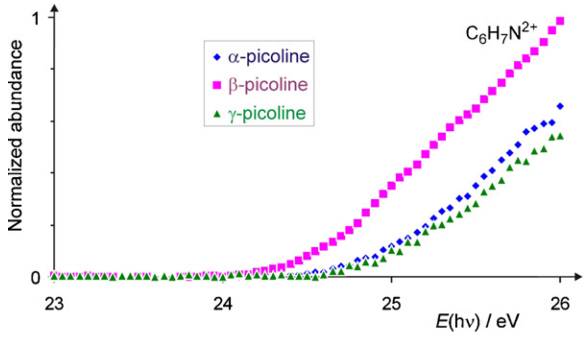


Fig. 3. Yields of the $C_6H_7N^{2+}$ dications formed upon photoionization of the isomeric neutral picolines as a function of the energy of the ionizing photons.

If we compare the vertical ionization energies for the formation of the triplet states of the picoline dications ${}^2IE_v{}^{0K}$ (values include correction for zero-point vibrational energy) with the experimental values, we find reasonable agreement for γ-picoline (${}^2IE_v{}^{0K,\gamma} = 24.63$ eV vs. ${}^2IE_{exp}{}^{\gamma} = (24.65 \pm 0.1)$ eV). The values determined for the β-picoline are also in acceptable agreement (${}^2IE_v{}^{0K,\beta} = 24.26$ eV vs. ${}^2IE_{exp}{}^{\beta} = (24.05 \pm 0.1)$ eV). For α-picoline, the theoretical vertical ionization energy is ${}^2IE_v{}^{0K,\alpha} = 24.21$ eV and the experimental ionization energy is ${}^2IE_{exp}{}^{\alpha} = (24.5 \pm 0.1)$ eV. The deviation between the theoretical and experimental values (${}^2IE_v{}^{0K,\alpha}$ vs. ${}^2IE_{exp}{}^{\alpha}$) is about the same as found for β-picoline, but notably the theoretical value ${}^2IE_v{}^{0K,\alpha}$ is very close to the energy calculated for β-picoline (${}^2IE_v{}^{0K,\beta}$), whereas the experimental ionization energy, ${}^2IE_{exp}{}^{\alpha}$, is closer to that of γ-picoline.

We have explored the possibility of autoionization processes populating the dicationic states. Specifically, the molecules may absorb a photon to populate states below the double ionization energy. These states then undergo a rearrangement to a structure with a lower ionization energy, and autoionize emitting one (or more) electron(s). For the picoline dications, the most straightforward rearrangement pathway is a migration of a hydrogen atom from the methyl group to the nitrogen atom. The resulting dications correspond to protonated pyridines with a methylene cation substituent (Fig. 4). The most stable arrangement is achieved, when the methylene cation is in the *meta*-position with respect to the nitrogen atom. At first glance, the occurrence of such an autoionizing process could explain why the β-picoline has a markedly lower ionization energy than α- and γ-picoline. However, the energetic data in Fig. 4 indicates such autoionization processes would be likely to lead to significantly lower double ionization energies (e.g., ${}^3\mathbf{5}^{2+}$ and ${}^1\mathbf{5}^{2+}$ are markedly stabilized with respect to $\mathbf{2}^{2+}$) than are observed in the experiment and this ionization pathway therefore considered unlikely.

The experimental appearance energies determined for the dehydrogenation pathways to the $[M–H_2]^{2+}$ dications are very similar for all isomers of picoline. The relevant structures of the dehydrogenated species are depicted in Fig. 5. The most straightforward dehydrogenation mechanisms are either a 1,1-elimination from the methyl group of the doubly ionized picoline to yield the fragments $\mathbf{F1}^{2+}$, $\mathbf{F2}^{2+}$, and $\mathbf{F3}^{2+}$, respectively, or a 1,2-elimination from the more stable methylenepyridinium dications ($\mathbf{4}^{2+}$, $\mathbf{5}^{2+}$, and $\mathbf{6}^{2+}$ in Fig. 4) in that hydrogen atoms are eliminated from the nitrogen atom and a neighboring carbon atom to yield the fragments $\mathbf{F4}^{2+}$, $\mathbf{F5}^{2+}$, and $\mathbf{F6}^{2+}$, respectively (Fig. 5).

Fig. 6 shows the relevant stationary points on the potential-energy surfaces associated with further hydrogen rearrangements in the dehydrogenated dications, as well as their rearrangements to the manifold of the azepine skeleton (**7**). Experimentally, the energies required for dehydrogenation amount to 0.8 eV, 0.95 eV, and 0.45 eV for the α-, β-, and γ-picoline dications, respectively.

According to our calculations, the direct elimination of H_2 from α-picoline dication (${}^1\mathbf{1}^{2+} \rightarrow {}^1\mathbf{F1}^{2+} + H_2$) requires an energy of 0.88 eV, which is in good agreement with the experimental value (0.8 eV). The energy demand of this dehydrogenation is about the same as the energy barriers associated with the hydrogen migrations to the ring. That is, as shown in Fig. 6, the energy barriers for hydrogen migrations are comparable to the energy of ${}^1\mathbf{F1}^{2+} + H_2$.

Table 1
Calculated adiabatic and vertical double ionization energies of α-, β-, and γ-picoline. The values highlighted in bold refer to the respective electronic state having the lowest energy.

	Singlet					Triplet				
	$^{2}IE_{\mathrm{a}}^{\mathrm{tot}}$[a]	$^{2}IE_{\mathrm{a}}^{\mathrm{0K}}$[b]	$^{2}IE_{\mathrm{v}}^{\mathrm{tot}}$[c]	$^{2}IE_{\mathrm{v}}^{\mathrm{0K}}$[d]	$\Delta^{2}IE_{\mathrm{v/a}}$	$^{2}IE_{\mathrm{a}}^{\mathrm{tot}}$[a]	$^{2}IE_{\mathrm{a}}^{\mathrm{0K}}$[b]	$^{2}IE_{\mathrm{v}}^{\mathrm{tot}}$[c]	$^{2}IE_{\mathrm{v}}^{\mathrm{0K}}$[d]	$\Delta^{2}IE_{\mathrm{v/a}}$
α-picoline	23.78	23.66	25.11	24.99	1.33	23.72	**23.56**	24.37	24.21	0.65
β-picoline	23.64	**23.49**	25.20	25.06	1.56	23.75	23.58	24.43	24.26	0.68
γ-picoline	24.24	24.10	26.09	25.95	1.86	24.10	**23.90**	24.84	24.63	0.74

[a] Calculated from total electronic energies for the optimized structures.

[b] Calculated from energies of the optimized structures including zero-point vibrational energies (ZPVEs).

[c] Calculated from total electronic energies of the optimized neutral picolines and the respective dications with the same geometry as optimized for their neutral counterparts.

[d] Same as c, but energies were corrected with ZPVEs calculated for the optimized structures neutral and doubly charged picolines.

However, the direct elimination of H_2 is expected to be kinetically favored to the rearrangements, because the rearrangements proceed via tight transition structures. Therefore, either dehydrogenation or retention of the α-picoline structure of dications is expected. In contrast, hydrogen migrations in β-picoline dication proceed over energy barriers which lie much lower than the dissociation limit for H_2 elimination ($^{1}\mathbf{F2}^{2+}+\mathrm{H}_2$). From the β-picoline structure the calculated energy required for the elimination of H_2 ($^{1}\mathbf{2}^{2+}\rightarrow{}^{1}\mathbf{F2}^{2+}+\mathrm{H}_2$) amounts to 2.22 eV, which is considerably higher than the experimental value of 0.95 eV. This discrepancy implies that the initially formed dication ($^{1}\mathbf{2}^{2+}$) rearranges to form the more stable species $^{1}\mathbf{5}^{2+}$ (3-methylenepyridinium dication), which consequently undergoes 1,2-elimination to form $\mathbf{F5}^{2+}$. The overall energy required for the loss of H_2 via this reaction pathway amounts to 1.15 eV. Alternatively, given the energy available, a rearrangement to the manifold of the azepine dications is also possible and then the most stable dehydrogenation product $\mathbf{F7}^{2+}$ can be formed.

A situation similar to β-picoline is also found for the γ-picoline dication, where the energy barriers for rearrangements are lower than that of direct H_2 elimination. The experimental energy determined for the H_2 elimination should thus correspond to the highest energy barrier on the pathway towards the azepine dication $\mathbf{7}^{2+}$, which can easily lose an H_2 molecule. The largest barrier corresponds to the initial hydrogen rearrangement from the methyl group to the *ipso*-position of the ring ($^{1}\mathbf{19/3}^{2+}$). The energy required for the dehydrogenation could thus be estimated as 0.84 eV. The experimental value 0.45 eV is lower than the theoretical threshold, but it should be noted that the dications are already, at threshold, generated in a vibrationally excited state, as discussed above,

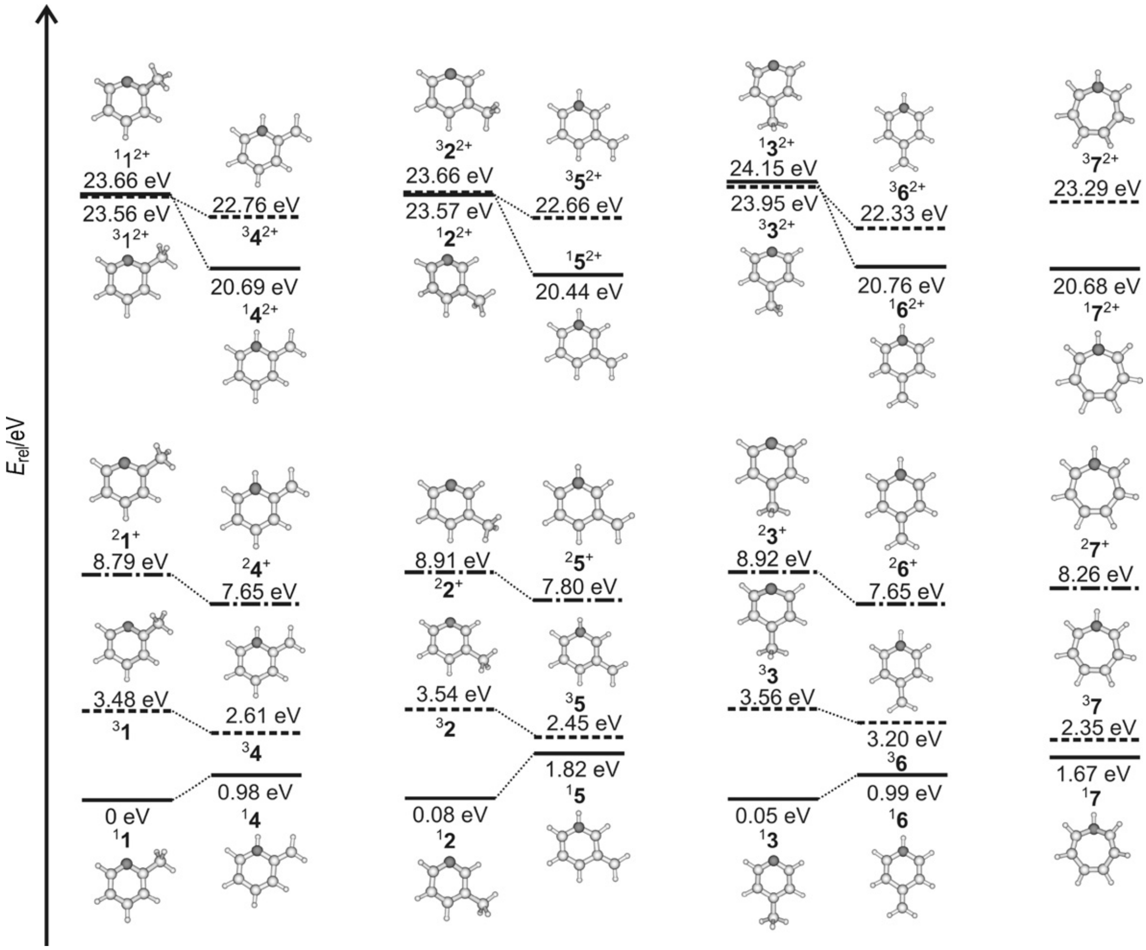


Fig. 4. Energy diagram for single and double ionization of α-, β-, and γ-picolines (**1**, **2**, and **3**, respectively) and azepine (**7**). With **4**, **5**, and **6** we indicate the isomers obtained by migration of an H atom from structures **1**, **2**, and **3**, respectively. The solid lines indicate singlets, dashed lines triplets, and the dash/dot lines doublets.

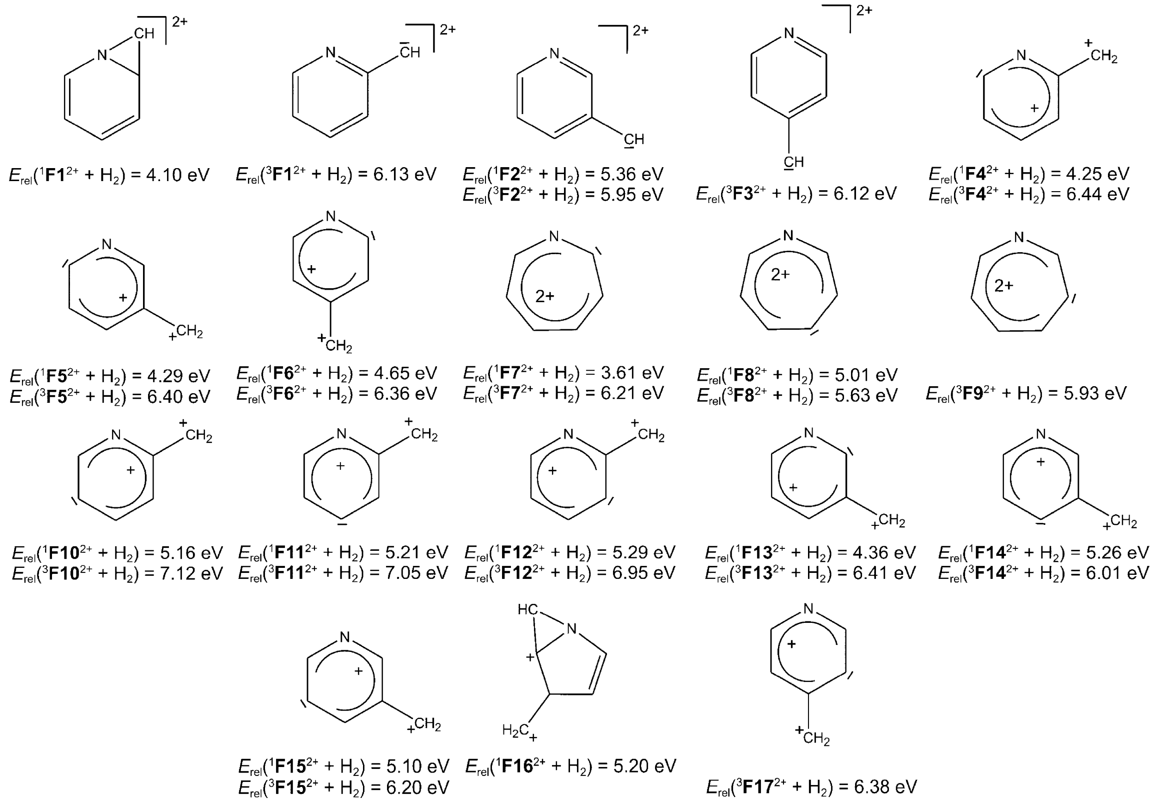
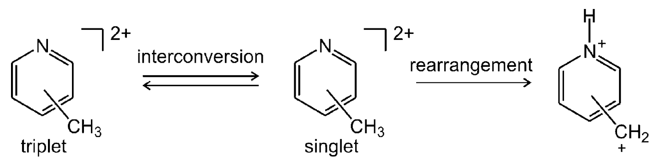


Fig. 5. Possible isomers of $C_6H_5N^{2+}$ formed upon dehydrogenation of α-, β-, and γ-picoline, respectively. In order to distinguish the dehydrogenated ions from the $C_6H_7N^{2+}$ parent ions, we use in notations an F-prefix (for "fragment"). The energies are given at 0 K relative to $E^{0K}(^1\mathbf{5}^{2+}) = -286.823527$ Hartree.

and therefore less additional energy is required to overcome the energy barriers for the rearrangements. The overall dissociation ($^1\mathbf{3}^{2+} \rightarrow {}^1\mathbf{F7}^{2+} + H_2$) is exothermic by 0.35 eV.

It is to be noted that the picoline dications are generated as a mixture of dications in the singlet and triplet states. The low energy barriers for rearrangements on the singlet potential energy surface of β-picoline dication ($^1\mathbf{2}^{2+}$) lead to a fast isomerization and dominant population of the most stable isomer $^1\mathbf{5}^{2+}$. As a result, the initially formed $^3\mathbf{2}^{2+}$ will be rapidly depleted by the interconversion [34] and subsequent isomerization on the singlet potential energy surface (Scheme 1). In comparison to β-picoline, the energy barriers for the rearrangements of the singlet γ-picoline dications are larger, although still not prohibitive (see above), and thus less efficient depletion of the triplet state dications can be expected in this case. Finally, the α-picoline dications represent a contrasting case to the β-picoline dications, in that the energy barriers for the rearrangements are high and the depletion of the triplet state via the interconversion-rearrangement mechanism will thus be slow (the second step in Scheme 1 is slow). In general agreement with the above arguments, the amount of H_2 elimination observed experimentally is much larger for dications generated from β- and γ-picoline compared to those generated from α-picoline.



Scheme 1. Depletion of the triplet state of the picoline dication ($^3\mathbf{1}^{2+}$, $^3\mathbf{2}^{2+}$, or $^3\mathbf{3}^{2+}$) via the interconversion to the singlet state ($^1\mathbf{1}^{2+}$, $^1\mathbf{2}^{2+}$, or $^1\mathbf{3}^{2+}$) followed by the rearrangement to a more stable $C_6H_7N^{2+}$ isomer (e.g., $^1\mathbf{4}^{2+}$, $^1\mathbf{5}^{2+}$, or $^1\mathbf{6}^{2+}$, respectively).

The structures of the dications generated upon ionization of the isomeric picolines were probed further using collision experiments. Here, the dications were generated by electron ionization of the neutral picolines [11,12]. At first sight, all three dications can be differentiated by their metastable ion (MI [35]) and collision induced dissociation (CID) spectra, which provides direct proof that the isomeric ions do not undergo equilibration to a common dication structure or a common mixture of ions [5,36]. In the metastable ion (MI) spectrum of α-picoline (Fig. 7(a)), the most abundant fragmentation corresponds to the loss of the methyl group (*m/z* 15) associated with the formation of $C_5H_4N^{+\bullet}$ (*m/z* 78). The second most intense process corresponds most probably to the elimination $HCN^{+\bullet}$ (*m/z* 27) together with formation of $C_5H_6^{+\bullet}$ (*m/z* 66). The third most important channel leads to the formation of $C_2H_4N^+$ (*m/z* 42) and $C_4H_3^+$ (*m/z* 51). In addition to the charge-separation channels, we also observe the loss of H_2 as mentioned already above. The CID spectrum (Fig. 7(b)) of the α-picoline dication is rather similar, with the exception of a more abundant fragmentation leading to the peak with *m/z* 51 and a small amount of charge transfer with xenon. The increased intensity of the ion at *m/z* 51 is presumably due secondary loss processes, namely loss of $CH_3^\bullet$ from the primary fragment $C_5H_6^{+\bullet}$ (*m/z* 66) or a loss of HCN from the fragment $C_5H_4N^{+\bullet}$ (*m/z* 78).

The MI results for β-picoline immediately reveal a dominant fragmentation leading to the charge-separation fragments $HCNH^+$ (*m/z* 28) and $C_5H_5^+$ (*m/z* 65). This fragmentation suggests that a significant population of the rearranged methylenepyridinium dication is sampled (see structures in Fig. 7). The second most intense dissociation channel is the same for all studied picoline isomers and corresponds to the loss of a methyl group. In contrast to α-picoline, the H_2 elimination channel is much more abundant for the β-picoline dication, and we can also observe elimination from the dication of a neutral fragment with a mass of 28 amu leading

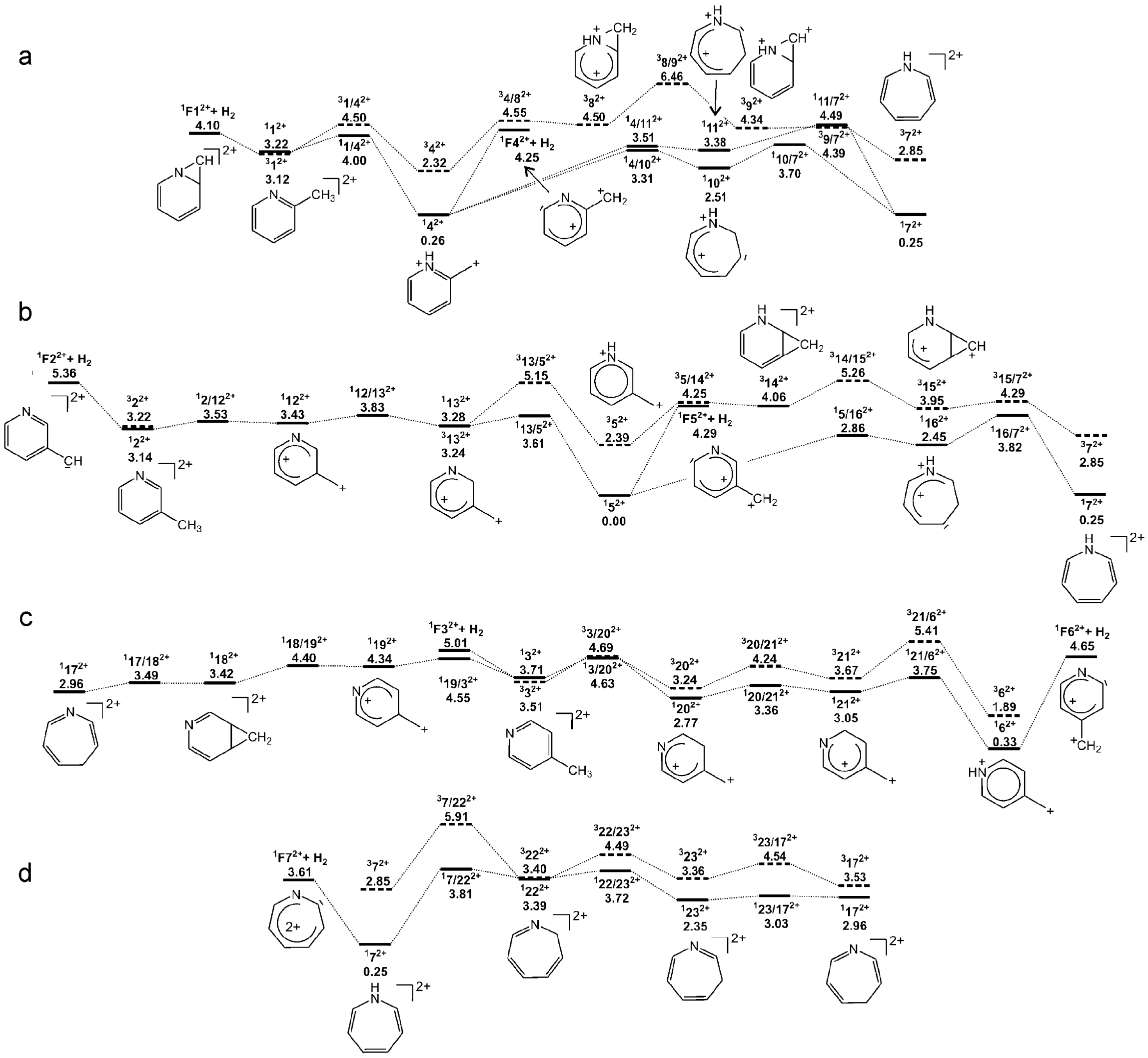


Fig. 6. B3LYP/6-311 + G(2d,p) potential energy surface for hydrogen and skeletal rearrangements of α-, β-, and γ-picoline dications (a, b, c, respectively) and azepine dication (d). All energies are given at 0 K relative to $E^{0K}(^1\mathbf{5}^{2+}) = -286.823527$ Hartree.

to an ion signal at *m/z* 32.5. The neutral fragment lost in this process most probably corresponds to ethylene. Finally, we observe a charge-separation channel leading to $C_3H_3^+$ (*m/z* 39) and $C_3NH_4^+$ (*m/z* 54). In collisions with xenon (Fig. 7(d)), again only a very small amount of electron transfer is observed. The channel in the MI spectrum leading to the ionic fragment with *m/z* 54 is suppressed in the CID spectrum, but the counterpart ions with *m/z* 39 have a larger abundance. These intensity changes can be explained by the depletion of the *m/z* 54 ions by a subsequent loss of a $CH_3^\bullet$ group, which leads to a fragment with *m/z* 39. In addition, we see abundant ions with *m/z* 51, which can be again due to a secondary dissociation of primary fragments, presumably by a loss of HCN from $C_5H_4N^{+\bullet}$ (*m/z* 78).

The fragmentation of γ-picoline to a large extent resembles that of β-picoline. However, there is a substantial difference in the intensity of the electron-transfer channel. In the CID studies of γ-picoline (Fig. 7(f)), electron transfer represents the dominant channel. The calculated recombination energies of the α-, β-, and γ-picoline dications and their isomers are listed in Table 2. The ionization energy of xenon is 12.13 eV. Given that, electron transfer proceeds via a Coulomb barrier, which usually roughly amounts to 2 eV [37–39], the recombination energy of the dication should be larger than 14 eV in order to see the occurrence of efficient electron transfer with xenon as a neutral reagent. Note that oxygen has similar ionization energy (12.07 eV) as xenon and therefore also efficient electron transfer between γ-picoline and background oxygen can be observed (even in the MI spectrum, Fig. 7(e)).

Given the recombination energies listed in Table 2, and the above arguments, we should observe electron transfer for all picoline dications having the same bond connectivity as the corresponding picoline neutrals, irrespective of their spin states. In contrast, the more stable rearranged isomers in their singlet ground states should not undergo electron transfer with xenon. Thus, we can suggest for γ-picoline that either a substantial population of the singlet dications does not rearrange or alternatively a large popula-

Table 2
Calculated adiabatic recombination energies (in eV) of an electron with α-, β-, and γ-picoline dications, their exo-methylenepyridinium dication isomers, and azepine dication.

	Singlet	Triplet
α-picoline dication ($\mathbf{1}^{2+}$)	14.87	14.77
β-picoline dication ($\mathbf{2}^{2+}$)	14.67	14.75
γ-picoline dication ($\mathbf{3}^{2+}$)	15.23	15.03
2-exomethylenepyridinium dication ($\mathbf{4}^{2+}$)	13.05	15.12
3-exomethylenepyridinium dication ($\mathbf{5}^{2+}$)	12.63	14.85
4-exomethylenepyridinium dication ($\mathbf{6}^{2+}$)	13.12	14.68
Azepine dication ($\mathbf{7}^{2+}$)	12.42	15.03

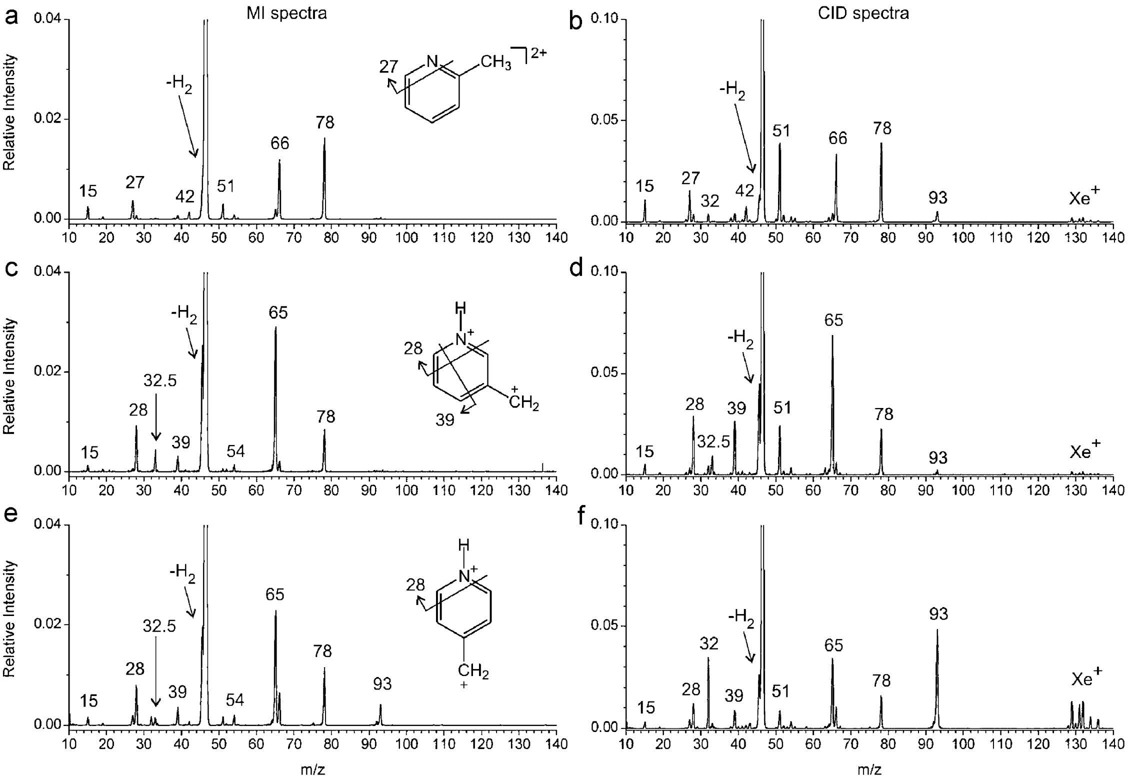


Fig. 7. Metastable ion (MI) spectra and collision induced dissociation (CID) spectra of α- (a and b), β- (c and d), and γ-picoline (e and f). The collision energy was 3.7 eV in the center-of-mass scale, the potential of the octopole during measurements of the MI spectra was identical. The numbers denote the mass-to-charge ratio (*m/z*) of the leading peak in a given group of peaks.

tion of the triplet state is formed and these triplets do not undergo a ready spin-flip to the singlet state. According to the rationale for H_2 elimination, which is based on the efficient rearrangement of the singlet γ-picoline dication, the formation of a large population of long-lived triplet states seems the viable explanation (see also the explanation above).

Similarly to the above arguments for γ-picoline, the increased amount of the radical-type fragmentations observed for the α-picoline dication can be explained by a larger population of the triplet state of the dication. This finding is furthermore in agreement with the fact that we find the triplet states to be the ground states for α- and γ-picoline dications (Table 1). The question however remains, why dications generated from α-picoline do not yield abundant electron transfer with xenon. The exothermicity of electron transfer between α-picoline dication in the triplet state and xenon amounts to 2.64 eV, whereas exothermicity of electron transfer between γ-picoline dication in the triplet state and xenon amounts to 2.90 eV. The energy difference between these two channels could be decisive for the ratio between the charge separation to $HCN^{+\bullet}$ and $C_5H_6^{+\bullet}$ on one hand and electron transfer on the other. The lower exothermicity, and thus lower efficiency, of electron transfer for α-picoline dication might thus lead to a marked preference for the competing charge-separation.

In contrast, the fragmentations of β-picoline are consistent with the dominant formation of dications in the singlet state, these dications then rearranging to structures which cannot electron transfer with Xe. Specifically, the most abundant channel is the charge separation to $HCNH^+$ and $C_5H_5^+$, whereas the radical cleavage to $HCN^{+\bullet}$ and $C_5H_6^{+\bullet}$ is almost completely suppressed. This explanation is fully consistent with the facile rearrangement of the singlet β-picoline dication proposed above to facilitate the ready elimination of H_2 from the β-picoline dication.

Finally, we return to the initial finding of the experimental double ionization energy of β-picoline being significantly lower than those determined for α- and γ-picolines. As discussed above and elsewhere [4], the experimental determination of the double ionization energy is very strongly influenced by the associated Franck–Condon factors. If the formation of the singlet states of the picoline dications is associated with unfavorable Franck–Condon factors, this may lead to increased uncertainties in the experimental determination of their double ionization energies. As indicated by the comparison of theoretical and experimental values above, the experimental thresholds may in fact be somewhat larger than the actual adiabatic ionization energies. Moreover, the fact that β-picoline dication has a singlet ground state, whereas α- and γ-picolines have triplet ground states could well be reflected in markedly different Franck–Condon envelopes and thus differences in the values of their double ionization thresholds extracted from experiment.

4. Conclusions

We have determined the double ionization energy of β-picoline as (24.05 ± 0.1) eV and the threshold energy for dehydrogenation of the dication as (25.0 ± 0.1) eV. The ionization energy is significantly lower than the previously determined double ionization energies of α- and γ-picoline, whereas all dications have similar energy threshold for dehydrogenation. We have performed additional MS/MS experiments with dications generated from all α-, β-, and γ-picolines, and complementary DFT calculations, in order to rationalize these results. As a result of these investigations we propose that α-picoline dication is generated mostly in the triplet state and does not undergo rearrangements, whereas the dications generated from β-picoline are mostly formed in the singlet state and undergo facile rearrangement. The proposed fate of dications generated from β-picoline are deduced from the more abundant H_2 loss from the β dication than the other picolines and the formation of closed-shell fragments in the charge-separation of the β-dication. Finally, γ-picoline dications are generated as a mixture of triplet and singlet states. Dications in the singlet states undergo rearrangements and dehydrogenation, whereas dications in the triplet state electron transfer readily with xenon in collisional experiments or undergo radical cleavage during metastable fragmentation. The differences in the double ionization energies derived from the experimental photoionization data cannot be fully explained by the calculated energetics. However, we would expect that unfavorable Franck–Condon factors associated with the double ionization of the title compounds would substantially affect the extraction of experimental double ionization energies for these species, complicating the inter-comparison of the experimental energies and the direct comparison with calculated values.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.07.027.

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