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UV Photoelectron Spectroscopy Studies of the Diazaxylylenes Generated from Amino(hydroxymethyl)pyridines*

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Diazaxylylenes generated by 1,4-elimination of water from amino(hydroxymethyl)pyridines under flash vacuum thermolysis (FVT) conditions can be directly studied by the UV-photoelectron spectroscopy (UV-PES). The elimination of water from these compounds starts at 450°C and is completed at 500–550°C. The interpretation of UV-photoelectron spectra was supported by Density Functional Theory studies.

Key words: UV photoelectron spectroscopy, amino(hydroxymethyl)pyridines, flash vacuum thermolysis, DFT calculations, ionization potential

Quinone methides (*ortho*-xylylenes) and iminoquinone methides (aza-*ortho*-xylylenes) are potential building blocks for the construction of condensed six-membered carbo- and heterocyclic systems, respectively. The chemistry of these reactive 1,3-dienes and their aza-analogues has been recently a subject of numerous reviews [2–4]. Contrary to aza-*ortho*-xylylenes, their diaza analogues, in which the nitrogen atom replaces a carbon atom in the ring (we named them diazaxylylenes for brevity), focused much less attention. There are only few reports dealing with generation and reactions of diazaxylylenes. These reactive species were generated by 1,4-elimination of water from pyridine analogues of 2-aminobenzyl alcohol [5,6], base-induced 1,4-elimination of hydrogen fluoride from 3-amino-4-(trifluoromethyl)quinoline [7] or thermal extrusion of sulfur dioxide from 1,3-dihydroisothiazolo[4,3-*b*]pyridine 2,2-dioxides [8,9]. The diazaxylylenes enter Diels-Alder reaction leading to 1,2,3,4-tetrahydro-1,5-naphthyridine derivatives [9].

*Orth*o-xylylenes were subject of theoretical studies, which enabled a closer insight on their reactivity. The most important from the synthetic point of view processes involving xylylenes are [4+2] cycloadditions. These reactions are governed by the difference between the energy of HOMO and LUMO of both diene and dienophile.

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Therefore, also in the case of the diaza analogues the determination of the energy of their frontier orbitals is important. Thoroughly discussed in the aza-xylylene chemistry were other processes: the valence isomerization leading to benzoazetine [10,11] and [1,5]-hydrogen shift leading to vinylanilines [12] or Schiff bases [13]. The driving force of all of these processes is recovery of the aromaticity by the six-membered ring.

In our previous papers we have shown that flash vacuum thermolysis combined with ultraviolet photoelectron spectroscopy (UV-PES) is a good tool for characterization of the electronic structure of aza-*ortho*-xylylenes generated by extrusion of sulfur dioxide from benzosultams [14] or by thermal retro-Diels-Alder reaction of 1,2,3,4-tetrahydroquinoline [11]. We were interested how the replacement of carbon atom in the ring in azaxylylene by nitrogen would influence the electronic properties of this reactive diene. In this report we present results of our studies on application of UV-PES to diazaxylylenes generated by the flash vacuum thermolysis of differently substituted amino(hydroxymethyl)pyridines. In order to determine the relative stability and the barriers of isomerization of envisaged species, we undertook also theoretical studies. Since, due to insufficient treatment of the correlation effects with HF/MP2 level, some problems were stressed previously [10,14], we decided also to apply density functional theory (DFT).

EXPERIMENTAL

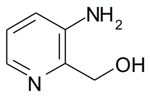
Starting materials: The investigated compounds were obtained from the corresponding ethyl esters of aminopyridinecarboxylic acids by the standard reduction with $LiAlH_4$ in tetrahydrofuran.

UV-Photoelectron Spectra: The photoelectron spectra were recorded on a Helectros 0078 instrument equipped with an 127° cylindrical analyser and monitored by a micro-computer supplemented with a digital analogue converter. The spectra were calibrated on the known auto-ionization of helium at 4.98 eV and nitrogen ionization at 15.59 eV. The short path thermolysis system was described elsewhere [15].

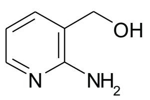
Computational methods: The calculations were performed using *Gaussian 98* program package [16]. The optimization and vibrational analysis were carried out with the density functional theory (DFT) [17] using BP86 [18] functional in conjunction with a 6-311G(d,p) basis set. The latter was also applied to the calculations of transitient states and ionic states. Also, the calculations at RHF/6-311G(d,p) level of theory with inclusion of dynamic electron correlation at the MP2 were done for comparison. Graphical representation of the nature of the molecular orbitals were obtained using a MOLDEN program [19].

RESULTS AND DISCUSSION

From the variety of methods available for the generation of aza-xylylenes, we have chosen the thermal elimination of water from compounds **1** and **2**. In this case, the sharp band corresponding to water (12.62 eV) should not interfere with the bands of the products. The elimination of water in our FVT conditions (from 10^{-3} to 10^{-4} mm Hg) starts at 450°C and is completed at 500–550°C. At this temperature well-differentiated spectra were obtained (Figure 1).



1



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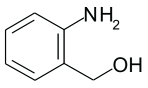

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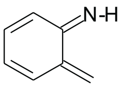

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The ionization potentials of the starting materials and the generated products are summarized in Table 1, in which for comparative purposes, the IPs of 2-aminobenzyl alcohol and aza-*ortho*-xylylenes are also included.

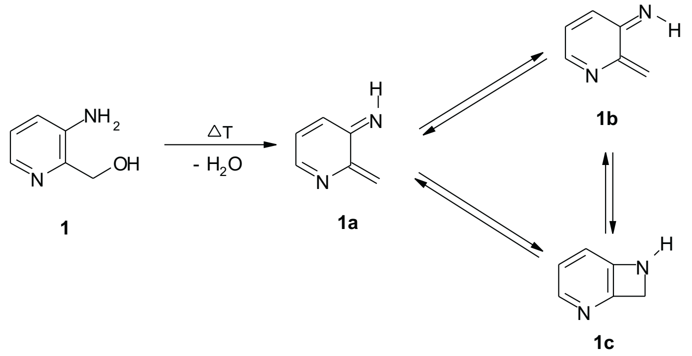
Table 1. Ionization potentials of amino(hydroxymethyl)pyridines and diazaxylylenes, compared with IPs of 2-aminobenzylalcohol and aza-*ortho*-xylylene.

	Precursor					Products			
	IP$_1$	IP$_2$	IP$_3$	IP$_4$		IP$_1$	IP$_2$	IP$_3$	IP$_4$
1	8.3 (π_1)	9.3 (n_N)	9.9 (π_2)	10.6 (n_O)	**1a/1b**	8.5	8.5	9.4	10.3
2	8.3 (π_1)	9.5 (n_N)	10.0 (π_2)	10.8 (n_O)	**2a/2b**	8.6	9.0–9.3		10.5
3	7.9 (π_1)	9.0 (π_2)	10.4 (n_O)	–	**4**	8.3 (π_1)	9.6 (n_N)	10.6 (π_2)	–

The ionization potentials of the precursors can be attributed as follows: IP$_1$ corresponds to ejection of one electron from the π-orbital (antibonding combination of pyridine a_2 orbital with amino-nitrogen lone pair), the IP$_2$ corresponds to ionization of the lone pair of pyridine nitrogen atom, the IP$_3$ is attributed to the ejection of one electron from the second π-orbital (mainly b_2 of pyridine) and the IP$_4$ to the ionization of one electron localized on the lone pair of the oxygen atom.

For the attribution of the observed ionization potentials values obtained during FVT of **1** and **2**, it is necessary to take into account the formation of different isomers in the light of calculations of the respective stability of the latter and the corresponding ionization potentials. For the clarity we present our approach only for thermolysis products obtained from the precursor **1**. The elimination of water from **1a** starts above 450°C and we observed the changes in the spectrum, in which new signals appeared at 8.5, 9.4, and 10.3 eV, as well as a fine band at 12.62 eV, corresponding to ionization

Scheme 1



potential of water. No further changes in the spectrum were observed during heating above 550°C. At this temperature the bands corresponding to the starting material disappeared. During the thermolysis of **1** two isomeric diazaxylylenes **1a** and **1b** and bicyclic azetopyridine **1c** can be formed.

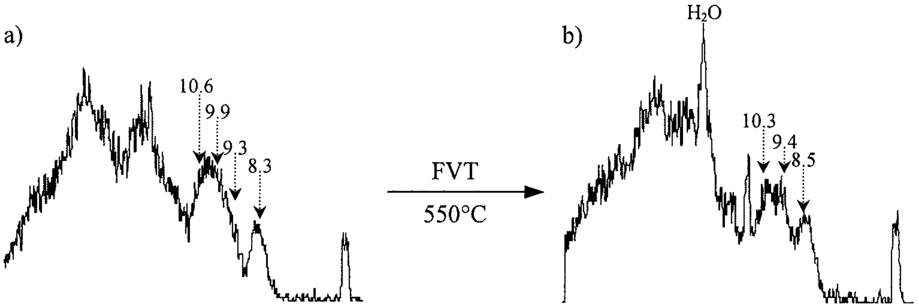


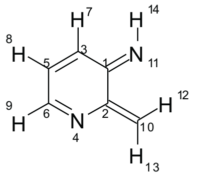
Figure 1. UV-PES spectrum of a) 3-amino-2-(hydroxymethyl)pyridine **1** and b) **1** at 550°C.

The calculations of geometrical parameters of three possible thermolysis products **1a–c** are collected in Table 2. The characteristic features of the calculated structures are twist of the *Z*-isomer **1b** from the plane, due to steric interactions by about 21°, completely planar *E*-isomer **1a** and serious internal stretch in the case of azetopyridine **1c**. It should be also stressed that the C10–N11 bond length in **1c** is unusually long comparing to a single C–N bond.

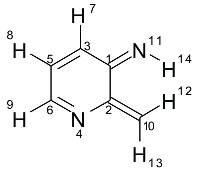
Since the elimination of water from 2-aminobenzyl alcohol under FVT conditions proceeds most likely by a six-centered transition state, the initially formed product would be **1a** and/or **1b**. Moreover, taking into account the thermal instability of benzocyclobutenes and benzoazetines, which at temperatures above 100°C undergo electrocyclic ring opening, the formation of azetopyridine **1c** under employed conditions seems to be very unlikely.

According to BP86/6-311G(d,p) calculations (Figure 2), *E*-isomer **1a** is more stable than **1b** by only 0.25 kcal·mol^{-1}, but the high energetical barrier for the isomerization of **1a** into **1b** (34.04 kcal·mol^{-1}) also excludes the formation of **1b** in favor to **1a**. In addition, taking into account the high energetical barrier for this electrocyclization (28.45 kcal·mol^{-1}), isomerization of **1a** into **1c** is also unfavorable. Considering that such low differences in the stability of isomers are strongly depended on the level of calculations, we checked and verified them at the HF/MP2/6-311G(d,p) level of theory, which revealed that the *Z*-isomer **1b** is more stable than *E*-isomer **1a** by 0.25 kcal ·mol^{-1}, but **1c** is more stable than **1a** and **1b** by 5.66 kcal·mol^{-1} and 5.41 kcal·mol^{-1}, respectively. Opposite tendency is observed when MP4 is employed. In this case **1a** is more stable than **1c** by 1.37 kcal·mol^{-1}. These calculations clearly show that electron correlation has to be included to obtain reliable results. Similar discrepancies were also noted for aza-*ortho*-xylylenes and benzoazetines, for which depending on the applied level of theory, calculations gave results from which the privileged structure was difficult to predict [10].

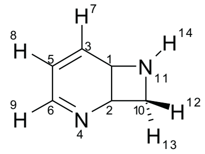
Table 2. Geometrical parameters and total energies of compounds **1a**, **1b**, and **1c**. BP86/6-311G(d,p).



1a



1b



1c

Parameters	**(1a)**	**(1b)**	**(1c)**
C(1)–C(2)	1.506 Å	1.506 Å	1.405 Å
C(1)–C(3)	1.467 Å	1.465 Å	1.390 Å
C(2)–N(4)	1.408 Å	1.409 Å	1.320 Å
C(3)–C(5)	1.357 Å	1.358 Å	1.416 Å
N(4)–C(6)	1.301 Å	1.301 Å	1.367 Å
C(5)–C(6)	1.458 Å	1.457 Å	1.405 Å
C(2)–C(10)	1.358 Å	1.358 Å	1.528 Å
C(1)–N(11)	1.299 Å	1.298 Å	1.428 Å
C(10)–N(11)			1.529 Å
C(2)–C(1)–C(3)	115.25°	114.95°	120.5°
C(1)–C(2)–C(10)	121.4°	121.1°	89.8°
C(1)–C(2)–N(4)	121.6°	121.0°	128.3°
C(2)–C(1)–N(11)	120.0°	127.2°	94.8°
C(1)–N(11)–C(10)			89.0°
C(2)–C(10)–N(11)			86.0°
C(10)–C(2)–C(1)–N(11)	–0.1°	–21.2°	5.2°
C(1)–C(2)–C(10)–H(12)	0.0°	–2.65°	109.6°
C(1)–C(2)–C(10)–H(13)	180.0°	179.7°	–118.2°
C(2)–C(1)–N(11)–H(14)	180.0°	–4.15°	–125.45°
C(4)–C(2)–C(1)–C(11)	–179.9°	162.1°	173.9°
C(3)–C(1)–C(2)–C(10)	179.9°	159.8°	–178.3°
C(2)–C(1)–N(11)–C(10)			–5.2°
E_{tot} (au)	–341.7769	–341.7765	–341.7804

Taking into account this difference on the isomers stability, it was essential to get more arguments. In other words, photoelectron spectra of **1a** and **1b** must be different.

Numerous works [20–25] have shown that ε_i^{KS} could be linked up to experimental ionization potentials (IP) by uniform shift $x = |-\varepsilon_i^{KS}\ (HOMO) - IP|$. This approach gives a remarkable agreement with experimental values and is justified by the fact that the first calculated vertical ionization potential IP, defined as the difference between E_T (cation) and E_T (neutral molecule), lies very close to experimental values. Stowasser and Hoffman [26] have recently shown that the localization of Kohn-Sham orbitals are very

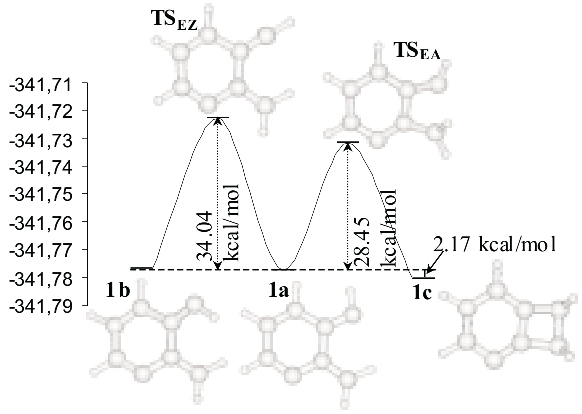


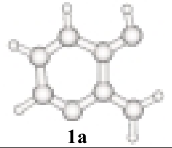
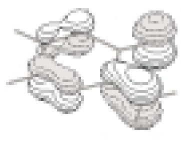
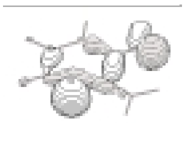
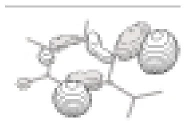
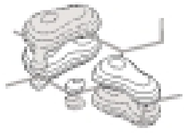
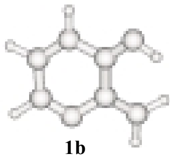
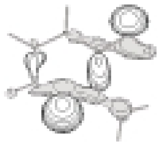
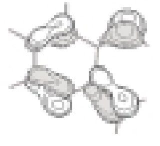
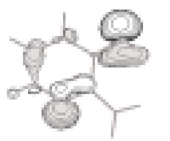
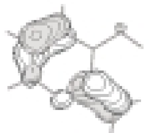
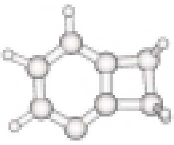
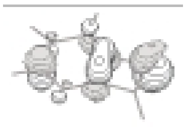
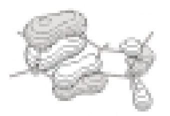
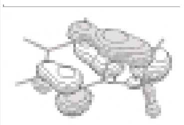
Figure 2. Calculated barriers of isomerization **1a** to **1b** and **1a** to **1c** [BP86/6-311G(d,p), total energies in au].

similar to those obtained after HF calculations. So it is possible to determine the nature of the first ionizations and to interpret unambiguously the photoelectron spectra.

Assignments of the obtained spectra were done on the basis of quantum calculations of Kohn-Sham energies (ε_i^{KS}), vertical ionization potentials (IP$_v$) using DFT, and Koopmans' orbital energies (ε_i) at MP2 level of theory. These results are presented in Table 3.

According to calculations for **1a** and **1b**, first two ionization potentials are in a very narrow region of 8.5–8.7 eV. Thus, the large band, observed at 8.5 eV, could correspond well to these assignments. Considering the case of **1c**, the first ionic state is calculated at 8.24 eV, but the energetic gap with the second ionization potential is estimated higher of *ca.* 0.6 eV. So, the large band observed experimentally at 8.5 eV corresponds better to **1a** or **1b**. An additional support for the open isomers **1a** and **1b** can be drawn from the comparison of the observed and calculated IPs with experimental values of 3-amino-2-picoline. In fact, in this case, the two first IPs at 8.2 and 9.3 eV are closer to those calculated for azetopyridine [11]. Therefore, we can reasonably attribute the first large band at 8.5 eV to the ejection of electrons from π-system in antibonding combination with the exocyclic $\pi_{C=N}$ and to the ejection from one electron from the σ system, principally localized on both nitrogen atoms lone pairs, respectively. The second band at 9.4 eV corresponds to the ejection of an electron from the bonding combination of the nitrogen atoms lone pairs, and the third at 10.3 eV to ionization of π-orbital.

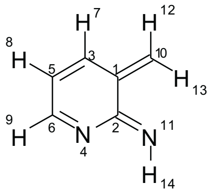
Table 3. The Kohn-Sham energies (ε_i^{KS}), vertical ionization potential (IP_v) and estimated ionization potentials IP_e at BP86/6-311G(d,p). In italics orbital energies (ε_i) at HF/MP2/6-311G(d,p) of **1a**, **1b**, and **1c**. For the comparison, experimental IP values of products obtained from **1** at 550°C are added. Molden visualization of the nature of Kohn-Sham orbitals is presented. All values are in eV.

 **1a**				
ε_i^{KS}	–5.81	–5.97	–6.68	–7.75
IP_e	IP_v = 8.51	8.67	9.38	10.45
ε_i	*–8.42*	*–11.26*	*–12.32*	*–11.03*
 **1b**				
ε_i^{KS}	–5.88	–5.97	–7.10	–7.79
IP_e	IP_v = 8.62	8.71	9.84	10.53
ε_i	*–11.19*	*–8.65*	*–12.96*	*–10.94*
 **1c**				
ε_i^{KS}	–5.36	–5.92	–6.75	–7.71
IP_e	IP_v = 8.24	8.80	9.63	10.59
ε_i	*–8.46*	*–11.28*	*–10.13*	*–12.36*
IP exp	**8.5 eV**	**8.5 eV**	**9.4 eV**	**10.3 eV**

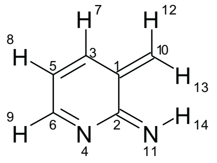
Products of the thermolysis of 2-amino-3-(hydroxymethyl)pyridine 2: The photoelectron spectrum of precursor **2** shows the bands at 8.25, 9.5 (shoulder), 9.9, and 10.9 eV. During the thermolysis at 510°C a very intense band corresponding to the ionization potential of water molecule (12.62 eV) appeared, accompanied of a new bands at 8.6, 9.2, and 10.5 eV. Similarly, as in the case of compound **1**, two isomeric diazaxylylenes **2a** and **2b** or azeto[2,3-*b*]pyridine **2c** can be formed.

Geometrical parameters and total energies of **2a**, **2b** and **2c** are presented in the Table 4.

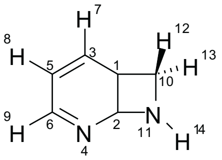
Table 4. Geometrical parameters and total energies of compounds **2a**, **2b**, and **2c** (BP86/6-311G(d,p)).



2a



2b



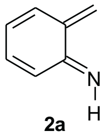
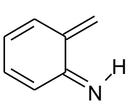
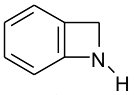
2c

Parameters	(2a)	(2b)	(2c)
C(1)–C(2)	1.506 Å	1.509 Å	1.410 Å
C(1)–C(3)	1.454 Å	1.457 Å	1.380 Å
C(2)–N(4)	1.419 Å	1.414 Å	1.324 Å
C(3)–C(5)	1.359 Å	1.358 Å	1.422 Å
N(4)–C(6)	1.301 Å	1.300 Å	1.366 Å
C(5)–C(6)	1.455 Å	1.459 Å	1.403 Å
C(1)–C(10)	1.358 Å	1.357 Å	1.526 Å
C(2)–N(11)	1.291 Å	1.293 Å	1.418 Å
C(10)–N(11)			1.522 Å
C(2)–C(1)–C(3)	117.1°	116.2°	119.6°
C(2)–C(1)–C(10)	121.6°	122.4°	88.7°
C(1)–C(2)–N(4)	119.8°	118.6°	129.0°
C(1)–C(2)–N(11)	119.95°	125.4°	95.5°
C(1)–C(10)–N(11)			86.7°
C(2)–N(11)–C(10)			88.6°
C(10)–C(1)–C(2)–N(11)	–0.2°	–27.6°	–5.8°
C(2)–C(1)–C(10)–H(12)	180.0°	177.2°	–109.2°
C(2)–C(1)–C(10)–H(13)	–0.03°	–4.4°	119.1°
C(1)–C(2)–N(11)–H(14)	180.0°	–3.3°	129.9°
C(3)–C(1)–C(2)–C(11)	179.8°	154.3°	175.1°
N(4)–C(2)–C(1)–C(10)	179.8°	154.4°	176.2°
C(2)–C(1)–C(10)–N(11)			5.3°
E_{tot} (au)	–341.7831	–341.7744	–341.7862

Like in the previously studied geometrical parameters of compound **1**, the *Z*-isomer **2b** has a twist structure. The bond angles of azetopyridine **2c** do not exceed 90.0° and the C10–N11 bond length in **2c** is always unusually long. According to the BP86/6-311G(d,p) calculations, azetopyridine **2c** is by 1.9 kcal·mol^{-1} more thermodynamically stable than **2a** and by 7.4 kcal·mol^{-1} more stable than **2b**. Employing HF/MP2/6-311G(d,p) level of calculations, azetopyridine **2c** is by 5.35 kcal·mol^{-1} more thermodynamically stable than **2a** and by 9.8 kcal· mol^{-1} more stable than **2b**.

The energies and estimated ionization potentials associated with Kohn-Sham orbitals of **2a**, **2b**, and **2c** are presented in Table 5. According to the estimated values of the four ionization potentials, the first large band can be reasonably assigned to the ionization of electrons from the two first molecular orbitals of **2a** and/or **2b**. The major difference is on the third ionization potential, which for **2a** and **2b** is expected near 9.0–9.3 eV and beyond 9.6 eV for **2c**. The fourth band at 10.5 eV also corroborates this hypothesis of **2a** and/or **2b** formation. Therefore, in our flash vacuum thermolysis reaction conditions, rather the formation of "open" isomers **2a** and/or **2b** can be postulated, but taking into account the calculated energetical stability data, the presence of isomer **2c** cannot be completely excluded.

Table 5. The Kohn-Sham orbitals energies and the calculated (BP86/6-311G(d,p)), estimated and experimental ionization potentials of **2a–c**.

		IP_1	IP_2	IP_3	IP_4
 **2a**	ε_I	–5.85 eV	–6.27 eV	–6.44 eV	–8.07 eV
	IP	8.54 eV (calcd)	8.96 eV (estd)	9.13 eV (estd)	10.76 eV (estd)
 **2b**	ε_I	–5.94 eV	–6.02 eV	–6.65 eV	–8.03 eV
	IP	8.69 eV (calcd)	8.77 eV (estd)	9.40 eV (estd)	10.78 eV (estd)
 **2c**	ε_I	–5.36 eV	–6.01 eV	–6.81 eV	–7.49 eV
	IP	8.22 eV (calcd)	8.87 eV (estd)	9.67 eV (estd)	10.35 eV (estd)
	IP_{exp}	**8.6 eV**	**9.0–9.3 eV**		**10.5 eV**

CONCLUSIONS

During thermal 1,4-elimination of water from 3-amino-2-(hydroxymethyl)pyridine **1** and 2-amino-3-(hydroxymethyl)pyridine **2** at about 500°C the formation of diazaxylylenes occurs. This hypothesis is corroborated by calculated and estimated values of ionization potentials. The obtained results are coherent with those obtained earlier for quinone methyleneimines and highlights the major thermodynamic instability of the investigated diazaxylylene system. A general remark may be formulated concerning the influence of nitrogen atom in the aromatic ring for the aza-*ortho*-xylylene system, which brings π-stabilization of about 0.2 eV compared to the benzene derivatives (Figure 3).

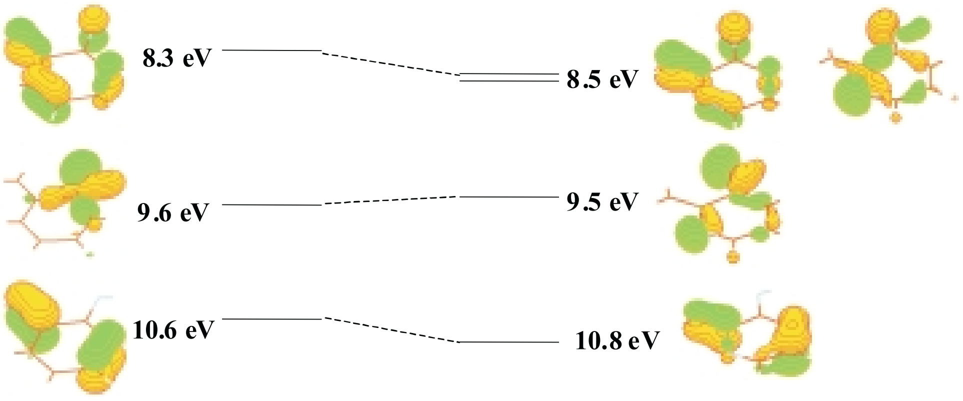


Figure 3. Nitrogen atom influence on the stability of aza-*ortho*-xylylene system. On the left: aza-*ortho*-xylylene **4**; on the right: aza-*ortho*-pyridoxylylene **1a**.

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