Application of Photoelectron Spectroscopy to Molecular Properties, 57[+]

UV Photoelectron Spectroscopy Studies of the Products of Thermal Extrusion of Sulfur Dioxide from Benzosultams

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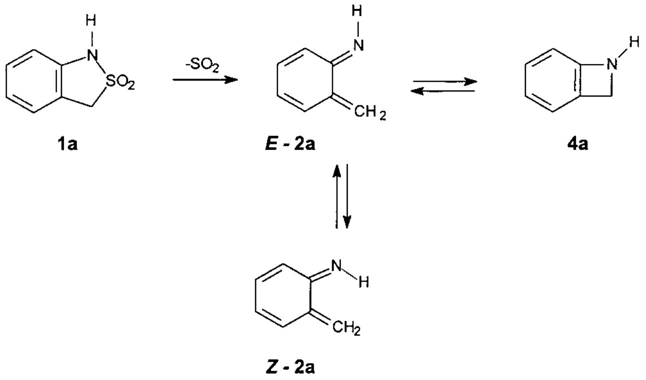
An aza-*ortho*-xylylene system is produced by thermal degradation of *N*-alkylbenzosultam, which can be directly studied by coupling the system to a UV/photoelectron spectrometer. These thermodynamically unstable xylylene derivatives rearrange to give aldimine by a [1,5] hydrogen shift.

Introduction

Aza-*ortho*-xylylenes, reactive 1-azadienes (6-methylene-2,4-cyclohexadien-1-imines), are potential intermediates in the synthesis of heterocyclic compounds.[2] These dienes can be generated by flash vacuum thermolysis of 2-aminobenzyl alcohols,[3] fluoride ion induced 1,4-elimination from 2-[(trimethylsilyl)amino]benzyltrimethylammonium salts,[4] or by photochemical[5] or thermal[6] extrusion of sulfur dioxide from 1,2-benzisothiazoline-2,2-dioxides (benzosultams). In the case of dienophiles, these azadienes undergo a [4+2] cycloaddition reaction leading to 1,2,3,4-tetrahydroquinoline derivatives,[6] while with nucleophilic agents, such as alcohols or amines, additions to the exocyclic methylene group occur leading to 2-aminobenzyl derivatives.[7] In the absence of a trapping agent various transformations of aza-*ortho*-xylylenes are possible. They can transform into aldimines[6] or *ortho*-vinylanilines[8] via a [1,5] hydrogen shift, or undergo dimerization[4] or polymerization.[7]

In the [4+2] cycloaddition reactions, the factor determining the course of the reaction is the difference between the energy of the HOMO and LUMO of both diene and dienophile. It is thus important to determine the energy of the aza-*ortho*-xylylenes' frontier orbitals. We suggest that the combination of flash vacuum thermolysis with ultraviolet photoelectron spectroscopy (UV/PES),[9] supported by theoretical studies, is a good way to confirm the electronic structure of these reactive intermediates.

In a previous paper,[10] we concluded on the basis of a photoelectron spectroscopic analysis supported by semi-empirical calculations (MNDO), that depending on the FVT temperature, the aza-*ortho*-xylylene formed from 2-aminobenzyl alcohol, 2-aminobenzylamine and 1,2,3,4-tetrahydroquinoline undergoes a valence isomerization leading to the benzazetidine **4a**. Sander,[11] however, has reported that during FVT or matrix photolysis of 2-aminobenzyl alcohol, 2-(diazomethyl)phenylamine, 2-methylphenylazide and 2-indolinone, no further valence isomerisation of the formed aza-*ortho*-xylylene, leading to benzazetidine **4a**, occurs.



Scheme 1

In this work we present our studies on UV/PES of the products generated by the flash vacuum thermolysis of differently substituted benzosultams **1a–g**. The interpretation of UV/photoelectron spectra is confirmed by the results of ab initio calculations.

Results and Discussion

Thermolysis of 1,2-Benzisothiazoline-2,2-dioxide (1a)

The photoelectron spectrum of precursor **1a** shows a first broad band at 8.8 eV, followed by a sharp signal at 9.7 eV,

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one broad band with two ionizations at 10.95 and 11.25 eV, and a broad, intense signal with a maximum at 12.1 eV. The bands at 8.8 and 9.7 eV correspond to the ionization of the electrons of the first two π-orbitals (an *ortho*-toluidine system stabilized by the electron-withdrawing effect of the SO_2 group), while the bands at 10.95, 11.25, and 12.1 eV correspond to the $4b_1$, $4b_2$, and $6a_1$ ionizations of the sulfoxide group.[12] The signal appearing at 11.5 eV can be assigned to the third π-ionization of *ortho*-toluidine (10.63 eV) localized on the nitrogen atom and stabilized by the SO_2 group.

The spectrum of the product formed during the thermolysis of **1a** at 520 °C (Fig 1b) reveals bands characteristic of an SO_2 group ionization. Nevertheless, we observed, as with the thermolysis of 2-aminobenzyl alcohol,[10] three bands at 8.3, 9.6, and 10.6 eV, accompanied by two bands at 7.8 and 8.8 eV whose relative intensities vary with temperature. We supposed that in the spectrum of the product of thermolysis of 2-aminobenzyl alcohol at 780 °C, the two unresolved bands of equal and low intensities at approximately 7.9 and 8.9 eV originated from unpyrolyzed starting compound.[10] For the **1a** precursor, thermolysis at 520 °C seems complete and in this case the unresolved ionization at 7.8−7.9 eV cannot be associated with the first band of starting material.

After closer investigation, we concluded that the ionizations at 7.8 and 8.8 eV can be attributed to a by-product formed during thermolysis. Solid stable material was deposited around the wall of the oven and the registered spectrum of this product shows two bands, one broad band at 7.8 eV and a second intense one at 8.8 eV. Can we associate the bands at 8.3, 9.6 and 10.6 eV with aza-*ortho*-xylylene or with benzazetidine? The only known isolog is the benzothiete.[13] In this case, the photoelectron spectrum (8.2, 9.3, and 10.3 eV) is similar to that of thiochroman[14] (7.8, 8.9, and 10.0 eV) with a slight shift to higher energies. Analogously, these ionizations could be compared to that of 2-mercaptotoluene[14] (8.3, 9.05, and 10.1 eV). We suppose the electronic structure of benzazetidine **4a** to be similar to that of *ortho*-toluidine, 1,2,3,4-tetrahydroquinoline and indoline. A prediction of the expected IP of **4a** can be made from the data available for the latter three compounds. The characteristic ionizations of 1,2,3,4-tetrahydroquinoline[10] are at 7.5, 8.5, and 10.1 eV. For the indoline[15] molecule IP′s are at 7.67, 8.90, 10.25 eV and those of *ortho*-toluidine[15] appear at 7.9, 8.5, and 10.6 eV. Thus, for the benzazetidine, the estimated ionization potentials should be close to 7.9 and 8.9 eV, and above 10.6 eV. The bands at 8.3, 9.6, and 10.6 eV observed during the thermolysis of 2-aminobenzyl alcohol and the sultam **1a** must be associated with the transient aza-*ortho*-xylylene **2a**. The oxygen analogue, 6-methylene-cyclohexa-2,4-diene-1-one, shows two ionization potentials at 8.8 and 10.65 eV associated to the ejection of the π-electrons of the ring, and at 9.4 eV corresponding to the ejection of one electron from the lone pair of the oxygen atom.[16] The former three values are close to those proposed for aza-*ortho*-xylylene. The by-product formed during the thermolysis of **1a** corresponds to the dimer of **2a**. Formation of a dimerization product was observed by one of us during the gas-phase thermolysis of benzosultams in a GC-MS system.[17]

The addition reaction of **1a** to the aza-*ortho*-xylylene **2a**, with further extrusion of SO_2, does not allow a shift of the equilibrium to permit the formation of benzazetidine. In the case of products obtained during the thermolysis of 2-aminobenzyl alcohol at high temperatures, the ionizations observed at 7.8 and 8.9 eV could be assigned to benzazetidine **4a**, but this unstable species may then undergo irreversible N−aryl bond cleavage. Thus, the observed high-temperature ionizations at 9.3 and 9.8 eV might be associated with the rearrangement product (benzaldimine or benzonitrile). Previous results[11] of ab initio calculations also corroborate this interpretation. The primary product **2a** is predicted to be more stable than **4a**, and at 600 °C the equilibrium lies far towards **2a**, in agreement with results from the FVP experiments.[11]

Taking into account Koopmans' approximation (polarisation effects are very important for the nitrogen lone pair), the calculated orbital energies for (*E*)-**2a** reasonably describe the experimental spectrum (−7.87, −10.71, −11.42, −11.55 eV).

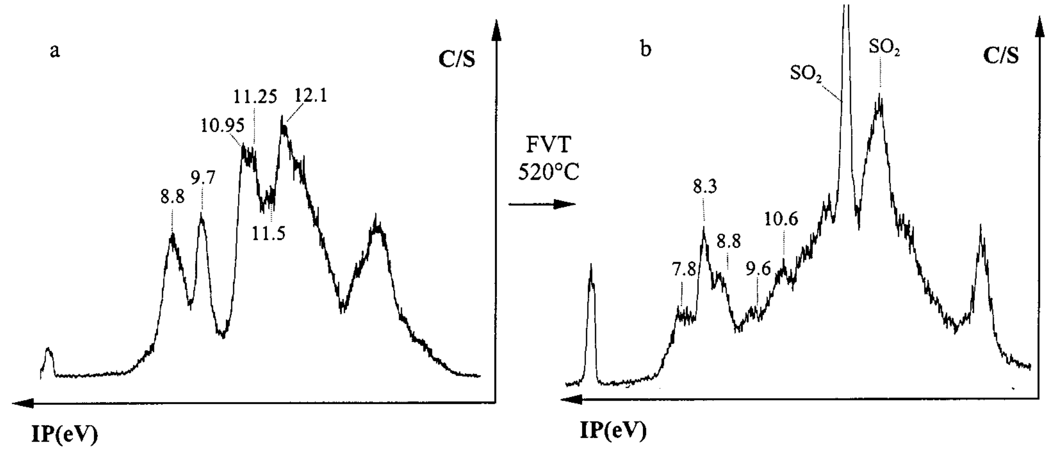


Figure 1. Photoelectron spectra of: (a): **1a**; (b): **1a** at 520 °C

Thermolysis of *N*-alkylbenzosultams

When the alkyl substituent is present on the benzosultam nitrogen atom, a [1,5] hydrogen shift can occur in the formed aza-*ortho*-xylylene resulting in formation of aldimine.[8] This intramolecular process is observed when the thermolysis of 4-, 5-, and 6-substituted 1-alkyl-benzosultams is performed in the absence of a trapping agent, and it prevails over the Diels−Alder reaction in the case of aza-*ortho*-xylylenes generated from 1-alkyl-7-substituted benzosultams.[6] In this case, a steric interaction between substituents in the position 7 and at the nitrogen atom forces the *Z*-configuration on the C=N bond favoring this suprafacial process. The values of IP of 1-alkylbenzosultams are collected in Table 1; their assignments are analogous to that of **1a**.

Table 1. Vertical ionization potentials IP_n (eV) of 1-alkylbenzosultams 1b−g

Cpd.	IP_1	IP_2	IP_3	IP_4
1b	8.35	9.55	10.6	11.0
1c	8.2	9.4	10.4	10.9
1d	8.1	9.3	10.3	10.7
1e	7.9	9.4	10.0	11.9
1f	8.85	10.1	11.2	
1g	8.75	10.1	10.9	

The thermolysis products of **1b**, **1d** and **1e** are presented in Figure 2. The spectra of the starting *N*-alkylbenzosultams **1b−d** are similar to that of the unsubstituted benzosultam **1a** presented in Figure 1.

The spectra of the products obtained after the thermolysis at 550°C are particularly well resolved. We observed three (or four) bands between 7.9 and 12.0 eV. If we compare the ionization potentials related to the product of thermolysis of **1b** with those discussed above for **1a**, it seems clear that the observed species cannot be the *N*-methyl de-

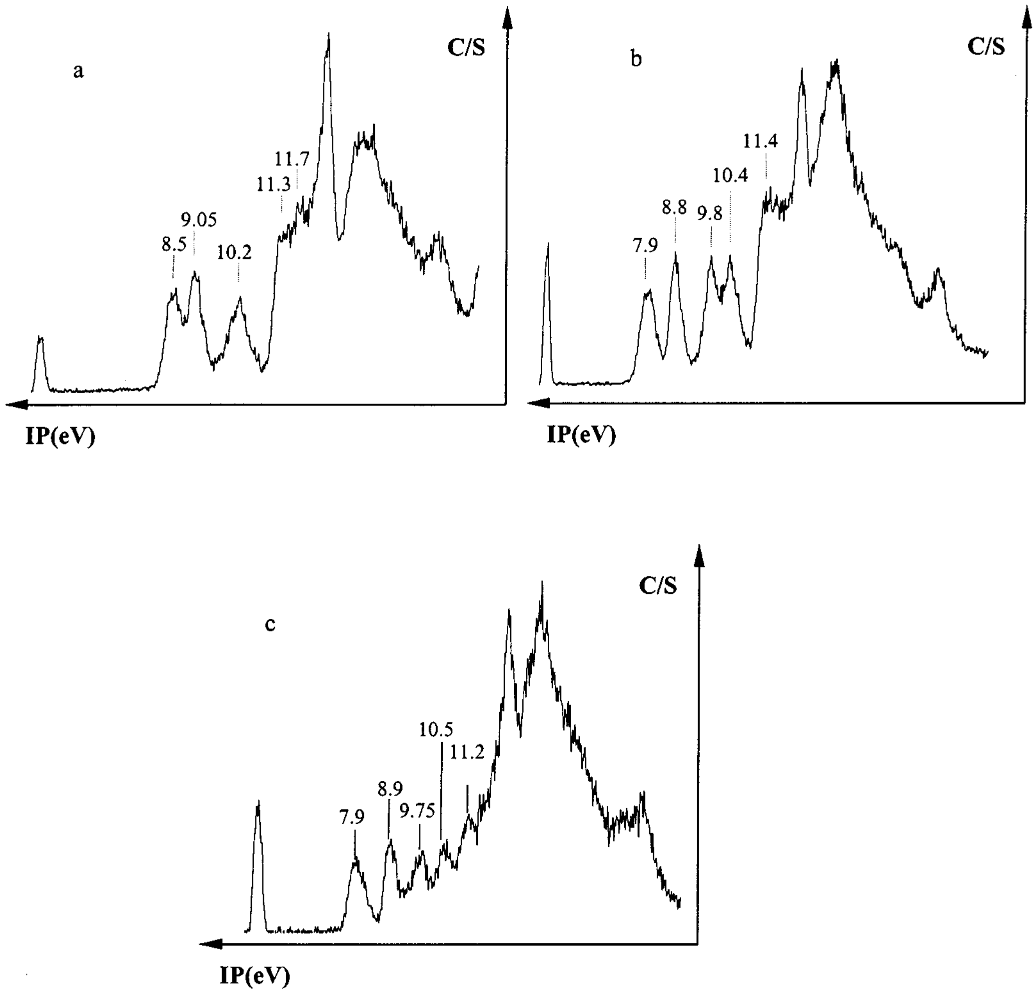
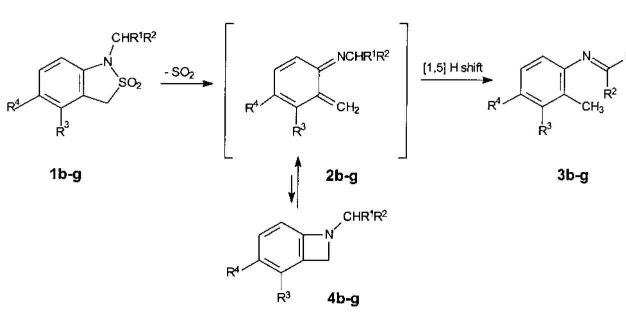


Figure 2. Photoelectron spectra of: (a): **1b** at 550°C; (b): **1d** at 580°C; (c): **1e** at 540°C



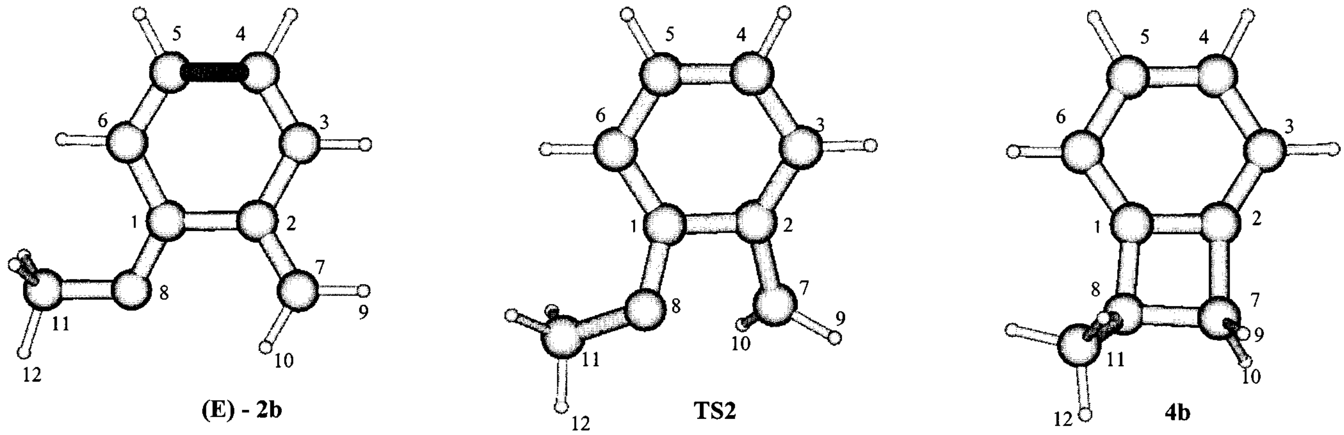
	R¹	R²	R³	R⁴
b	H	H	H	H
c	H	CH_3	H	H
d	CH_3	CH_3	H	H
e	H	H	H	OCH_3
f	H	H	NO_2	H
g	H	H	H	NO_2

Scheme 2

rivative of aza-*ortho*-xylylene **2b** since the first ionization potential appears at 8.5 eV (8.3 eV for **1a**).

Two ways of transformation of **2b** are possible, a ring closure leading to the benzazetidine **4b**, or a [1,5] hydrogen shift from the methyl group to the nitrogen atom resulting in the formation of Schiff base **3b**. The geometrical parameters of the isomeric structures (*Z*)-**2b**, (*E*)-**2b**, **3b** and **4b** were performed at the MP2 theory level using the 6−311G (d,p) basis set, and are collected in Table 2.

The energetically favored (by 1.7 kcal/mol) *E*-isomer of **2b** is nearly planar, while the *Z*-isomer of **2b** is twisted by about 30°. The benzazetidine **4b** has a benzenoid structure with the four-membered ring only slightly twisted (by 5.9°). At this level of approximation, compound **4b** is less stable than **2b** by 9.2 kcal/mol whereas **3b** is more stable than **2b** by 31.3 kcal/mol. For benzaldimine **3b** the phenyl ring is twisted by 51° relative to the imino group.



(E) - 2b

TS2

4b

Figure 3. Ab initio equilibrium structures of (*E*)-**2b**, **TS2** and **4b** calculated at the MP2/6−311 G(d,p) level; the numbering scheme corresponds to Table 2

The transition state TS_2 leading to the closure of the four-membered cycle (conrotatory process) is calculated to lie 25.8 kcal/mol above the *E*-isomer of **2b**. The transition state corresponding to the suprafacial [1,5] hydrogen shift lies 14.5 kcal/mol above the *Z*-isomer of **2b**. The geometrical parameters are presented in Table2.

According to our calculations, the aldimine **3b** is energetically highly favored and, at the temperatures used in our flash vacuum thermolysis experiments (T > 520°C), the reaction must be shifted to this isomer. In the photoelectron spectrum we observed three bands at 8.5, 9.05, and 10.2 eV. Taking into account Koopmans′ theorem, the calculated ionization energies for **2b**, **3b**, and **4b** fit only with the experimental IP′s of **3b**, although formation of **4b** cannot be completely excluded.

This ambiguity was clarified by a closer study of the effects of the substituent at the position 1 in benzosultam. The first two sharp and intense bands observed at 8.5 and 9.05 eV appear to be slightly destabilized in comparison with those of toluene (8.83 and 9.36 eV). This fact can be explained by weak interactions between the phenyl ring and the π-orbital of the imino group (12.55 eV). The third ionization is associated with the ejection of an electron from the nitrogen lone pair. The observed IP value at 10.2 eV is coherent with n_N ionization of the methyleneimine (10.6 eV). The potentials at higher energies (11.3 and 11.7 eV), are close to the values of 11.43 and 11.98 eV observed for toluene. π-Ionization of the imino group (12.55 eV), which interacts weakly with the π-system of the phenyl ring, appears at higher energies. Substitution at the imine carbon in **3** causes the shift of these bands, which is in agreement with the formation of the aldimine molecule. For **3c** and **3d**, the first band was shifted by 0.25 and 0.6 eV, respectively. Taking into account Bock′s[18] values of the π-ionizations for the C-methylated and C,C-dimethylated imines (11.43 and 11.08 eV), this observation suggested a weaker interaction than for **3b** between the phenyl ring and the C-substituted imino group due to the steric hindrance. The second band localized on the phenyl ring is slightly sensitive to the sub-

Table 2. Structural parameters of **(*Z*)-2b**, **TS1**, **3b**, **(*E*)-2b** and **4b**, calculated at the MP2 level of theory with conjunction with the 6−311G(d,p) basis set

Parameter[a]	**(*Z*)-2b**	**TS1**[b]	**3b**	**(*E*)-2b**	**TS2**[c]	**4b**
C(1)−C(2)	1.301	1.433	1.410	1.496	1.421	1.397
C(1)−C(6)	1.465	1.442	1.403	1.466	1.411	1.391
C(1)−N(8)	1.301	1.317	1.418	1.2975	1.366	1.428
C(2)−C(3)	1.462	1.436	1.400	1.457	1.405	1.386
C(2)−C(7)	1.360	1.407	1.506	1.356	1.425	1.521
C(3)−C(4)	1.358	1.348	1.400	1.358	1.3945	1.410
C(4)−C(5)	1.452	1.431	1.397	1.452	1.418	1.407
C(5)−C(6)	1.359	1.345	1.398	1.361	1.395	1.408
C(7)−C(8)	3.122	2.878	2.827	2.813	2.170	1.512
N(8)−C(11)	1.451	1.343	1.282	1.459	1.466	1.458
C(1)−C(2)−C(7)	123.7	121.2	120.0	120.85	102.5	88.7
N(8)−C(1)−C(2)	129.1	121.9	117.9	117.9	105.4	95.5
C(1)−C(2)−C(3)	116.9	117.5	118.2	118.4	120.75	122.5
C(2)−C(1)−C(6)	115.6	118.3	120.7	16.2	120.8	123.5
C(1)−N(8)−C(11)	121.2	120.3	116.8	117.85	116.5	117.8
C(7)−C(2)−C(1)−N(8)	30.2	−16.12	2.9	−14.0	24.1	5.9
C(1)−C(2)−C(7)−H(9)	178.6	154.2	−169.6	178.4	−147.6	−120.25
C(1)−C(2)−C(7)−H(10)	3.05	−62.4	70.1	−1.1	54.8	107.5
C(2)−C(1)−N(8)−C(11)	3.8	19.05	−129.2	178.1	−146.8	−125.4
C(1)−C(2)−C(7)−N(12)	−45.75	27.45	−48.4	−	−	−
EUMP2	−363.9271	−363.90655	−363.97965	−363.9298	−363.8886	−363.9444

[a] Distances in Angstroms; bond angles and dihedral angles in degrees; total energies in ua. See Figure 3 for numbering. − [b] Transition state of the [1,5] hydrogen shift of **(*Z*)-2b** to give **3b**. − [c] Transition state of the ring closure of **(*E*)-2b** to give **4b**.

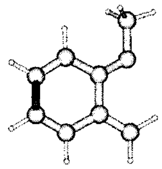
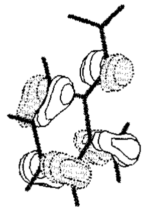
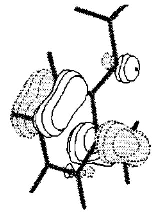
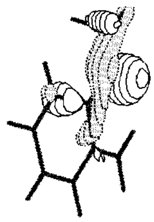
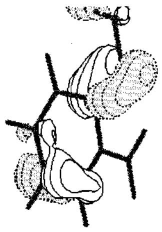
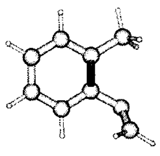
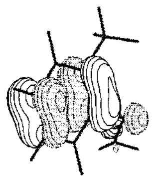
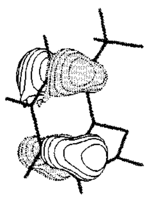
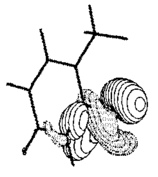
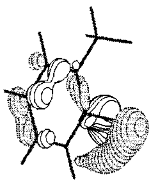
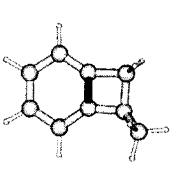
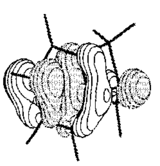
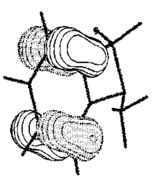
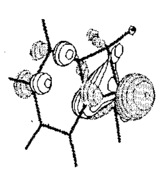
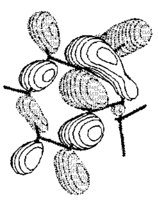
 **2b** **(E)** ε_i **(Z)** ε_i	 -7.70 -7.78	 -10.56 -10.52	 -10.67 -10.71	 -11.02 -11.12
 **3b** IP ε_i	 8.5 -8.41	 9.05 -8.96	 10.2 -11.64	 -12.13
 **4b** ε_i	 -8.07	 -9.06	 -11.08	 -12.61

Table 3. Graphical visualization of the molecular orbitals of **2b**, **3b** and **4b** calculated at the MP2 level of theory with conjunction with the 6−311G(d,p) basis set (IP and orbital energies ε_i in eV)

stituent effect. The third potentials are destabilized by 0.2 (**3c**) and 0.4 (**3d**) eV. These observed IP′s (10.0 eV and 9.8 eV) are consistent with n_N ionizations of ethylene- and isopropylidene-imine (10.17 and 9.95 eV respectively). A weaker interaction than in **3b** is also observed between the lone pair of the imine-nitrogen atom and the phenyl ring for this ionization potential. The ionization potentials at 10.9 (**3c**) and 10.4 (**3d**) eV can be assigned to the ionization of orbitals corresponding to nonbonding interactions of the π-system of the imino group with the totally symmetrical π-orbital of the phenyl ring. The band observed at 12.0 eV corresponds to an analogous bonding orbital. The results presented above support the formation of aldimines.

The photoelectron spectra obtained during the thermolysis of precursors substituted in the benzene ring by methoxy and nitro groups can be interpreted analogously. The IP′s observed for the 5-methoxy derivative **3e** (Figure 2c), particularly the first ones (7.9, 8.9, 10.5, and 11.2 eV), correspond to those of 3-methoxytoluene (8.3, 8.9, 10.75, and 11.3 eV) shifted to lower energies. Analogously, the ionization at 9.75 eV, attributed to the ejection of an electron from the nitrogen lone pair, is also markedly shifted to lower energies than in **3b**. This could be due to the more pronounced conjugation between the phenyl ring and the imino group. In the thermolysis of the nitro-substituted benzosultam **1f** at 480°C, the opposite effect is observed (9.1, 9.9, 10.5, 11.0 eV). Surprisingly, in the case of the photoelectron spectrum of aldimine **3g**, generated from **1g** at 520°C, we observed lower ionization potentials than with **3f** (9.0, 9.55, 10.6, 11.0 eV), which contradicted the IP values known for 2-nitrotoluene (9.63 and 9.90 eV) and 3-nitrotoluene (9.48 and 10.03 eV). Such behaviour could originate from steric hindrance in the *N*-(2-methyl-3-nitrophenyl)methylenimine **(3f)** (NO_2 group out-of-plane of the phenyl ring).

Conclusion

This investigation highlights the major thermodynamic instability of the aza-*ortho*-xylylene system. Generation of these species by thermal degradation of *N*-alkylbenzosultams at about 500°C favors the formation of aldimines due to the low activation barrier of the [1,5] hydrogen shift (ca. 15 kcal/mol). Thus, the more thermodynamically stable aldimines are uniquely characterized products.

Experimental Section

General Remarks: The investigated compounds were obtained according to the known procedures (**1a,**[19] **1b−e,**[20] **1f,**[21] **1g**[22]).

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 is described elsewhere.[23]

Computational Methods: Ab initio calculations were performed using Gaussian 94.[24] The optimization and vibrational analysis were carried out at a RHF/6−311G(d,p) level of theory with inclusion of dynamic electron correlation at the MP2 level. Graphical representations of the nature of the molecular orbitals were obtained using a MOLDEN program.[25]

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