

# Electronic Structure and Gas-Phase Thermolysis of Substituted Tetrazolines Studied by Photoelectron Spectroscopy

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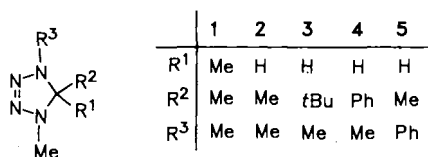
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The electronic structures and the gas-phase thermolyses of tetrazolines 1–5 have been studied by photoelectron spectroscopy. For compounds 1–4 cycloreversion to imine and methyl azide is observed, whereas compound 5 is contracted to give the respective diaziridine. To assign the PE spectra, MNDO calculations were performed for compounds 1, 2, 4, and 5; some conformational properties of 5 have also been studied by AM1 calculations.

Cyclic and acyclic 2-tetrazenes are valuable precursors of aminyl radicals and their reaction products like hydrazine derivatives<sup>1</sup>. Tetrazolines<sup>2,3</sup>, readily accessible from nitrilium salts and azides, accordingly might be converted into substituted diaziridines<sup>3,4</sup>. Continuing our studies on the electronic structures and thermal stabilities of 2-tetrazenes<sup>5</sup>, we have investigated five substituted tetrazolines (1–5) by variable-temperature photoelectron spectroscopy<sup>6,7</sup>.



## Electronic Structures of Tetrazolines 1–5

The PE spectra of tetrazolines 1–5 are depicted in Figure 1; the observed ionization potentials are collected in Table 1. With reference to the Koopmans approximation<sup>8</sup>,  $IP(i) = -\epsilon(i)$ , the ionization potentials are assigned to molecular orbitals. The assignments given are based on comparison with the PE spectra of other 2-tetrazenes<sup>5,9</sup> and MNDO<sup>10</sup> calculations for compounds 1, 2, 4, and 5. The relevant results of the calculations are summarized in Tables 2 and 3.

Tetrazolines consist of a *cis*-2-tetrazene group comprised in a five-membered ring, and their electronic structure can be expected closely to resemble the latter one's. 2-Tetrazenes are characterized by three occupied  $\pi$ MOs ( $\pi_1 - \pi_3$ ) and two  $n$  MOs ( $n_+$  and  $n_-$ )<sup>5,9</sup>. For the aliphatic tetrazolines 1–3, the orbital sequence is  $\pi_3$  (HOMO),  $\pi_2$ ,  $n^-$ ,  $n^+$ . In the aromatic compounds 4 and 5 one or two ionization bands of the phenyl group, assigned as  $\pi(\text{Ph})$ , are located between

## Photoelektronenspektren, elektronische Struktur und Gasphasenthermolysen von substituierten Tetrazolinen

Die elektronische Struktur und die Gasphasenthermolysen der Tetrazoline 1–5 wurden durch Photoelektronenspektroskopie untersucht. Die Verbindungen 1–4 zerfallen durch Cycloreversion in Methylazid und die entsprechenden Imine. Demgegenüber wird aus 5 unter Ringkontraktion ein Diaziridin gebildet. Zur Zuordnung der PE-Spektren wurden an den Verbindungen 1, 2, 4 und 5 MNDO-Rechnungen, zur Konformationsanalyse von 5 auch AM1-Rechnungen durchgeführt.

Table 1. Vertical ionization potentials [eV] of tetrazolines 1–5

<i>i</i>	$\pi_3$	$\pi_2$	$n_-$	$n_+$	$\pi(\text{Ph})$	
1	7.94	9.58	10.38	11.52		
2	8.38	9.86	10.74	11.93		
3	8.17	9.80	10.33	11.2		
4	8.20	10.00	10.73	11.67	9.14	9.54
5	7.77	10.25	10.85	11.8	9.15	

Table 2. Orbital energies  $\epsilon$  [eV] of tetrazolines 1, 2, and 4 (MNDO results)

	$-\epsilon$					$\pi(\text{Ph})$	
	$\pi_3$	$\pi_2$	$n_-$	$n_+$			
1	9.31	11.22	12.38	12.77			
2	9.60	11.32	12.51	12.97			
4	9.65	11.27	12.36	13.31	9.48	9.52	

Table 3. Heats of formation  $\Delta H_f$  [kJ/mol], torsional angle  $\Phi$  [°] and orbital energies  $\epsilon$  [eV] for different conformations of tetrazoline 5 (MNDO and AM1 results)

	$\Phi$	$\Delta H_f$	$\pi_3$	$\pi(\text{Ph})$	$\pi(\text{Ph})$	$-\epsilon$	$n_-$	$n_+$	$r^a$
						$\pi_2$			
MNDO	0 <sup>b</sup> )	310	8.99	9.62	10.11	11.69	12.40	12.87	0.973
	90 <sup>c</sup> )	300	9.37	9.67	9.77	11.37	12.46	12.80	0.951
AM1	0 <sup>b</sup> )	560	9.06	9.93	10.02	11.39	11.95	12.33	0.984
	23 <sup>d</sup> )	558	8.93	9.91	10.05	11.59	11.84	12.27	0.979
	90 <sup>c</sup> )	564	9.40	9.91	10.01	10.99	12.07	12.21	0.964

<sup>a</sup>) Correlation coefficient of orbital energies and ionization potentials (Table 1). — <sup>b</sup>) Conformer 5a. — <sup>c</sup>) Conformer 5b. — <sup>d</sup>) Conformer 5c.

those of  $\pi_3$  and  $\pi_2$ . For compound **4** the sequence of IPs (Table 1) does not coincide with that one of the calculated MO energies (Table 2). Obviously the aromatic  $\pi$ MOs are calculated more accurately than the MOs of the 2-tetrazene unit. It was not possible to identify ionizations caused by electrons from  $\pi_1$  since the corresponding bands are located in the unresolved  $\sigma$  part of the spectra ( $>11$  eV).

The variation of the IPs of tetrazolines **1–5** can be rationalized in terms of substituent perturbations. Additional alkyl groups destabilize both  $\pi$  and  $n$  MOs. This becomes evident when the IPs of **2** are compared with those of **1** and

**3**. The C-phenyl group in compound **4** is expected to exert a smaller effect than the *N*-phenyl group in compound **5**. Accordingly, compared with **2**, the IPs of **4** are shifted less than 0.3 eV while those of **5** deviate up to 0.6 eV.

In the spectrum of compound **4** two ionizations caused by  $\pi$  electrons of the phenyl group are discernible, while for **5** a single broad band of approx. double intensity is found. These ionizations are related to the MOs  $\pi_2$  and  $\pi_3$  of the aromatic rings. In **4** the IPs are close to those observed for toluene (8.83 and 9.36 eV)<sup>11</sup> indicating similar perturbations of the aromatic  $\pi$  systems by the substituents. The split of these two  $\pi$  levels is not reproduced by the MNDO calculation (Table 2). From the spectrum of **5** it follows that as a result of different interactions with the MOs of the tetrazoline ring, the two aromatic  $\pi$  orbitals are nearly degenerate.

The conformation of compound **5** is of particular interest. The phenyl group might either be parallel (**5a**) or perpendicular (**5b**) to the five-membered ring. In **5a** there would be strong interaction between the  $\pi$  electron systems of the 2-tetrazene and the phenyl group whereas in **5b** the two  $\pi$  systems would be orthogonal towards each other.

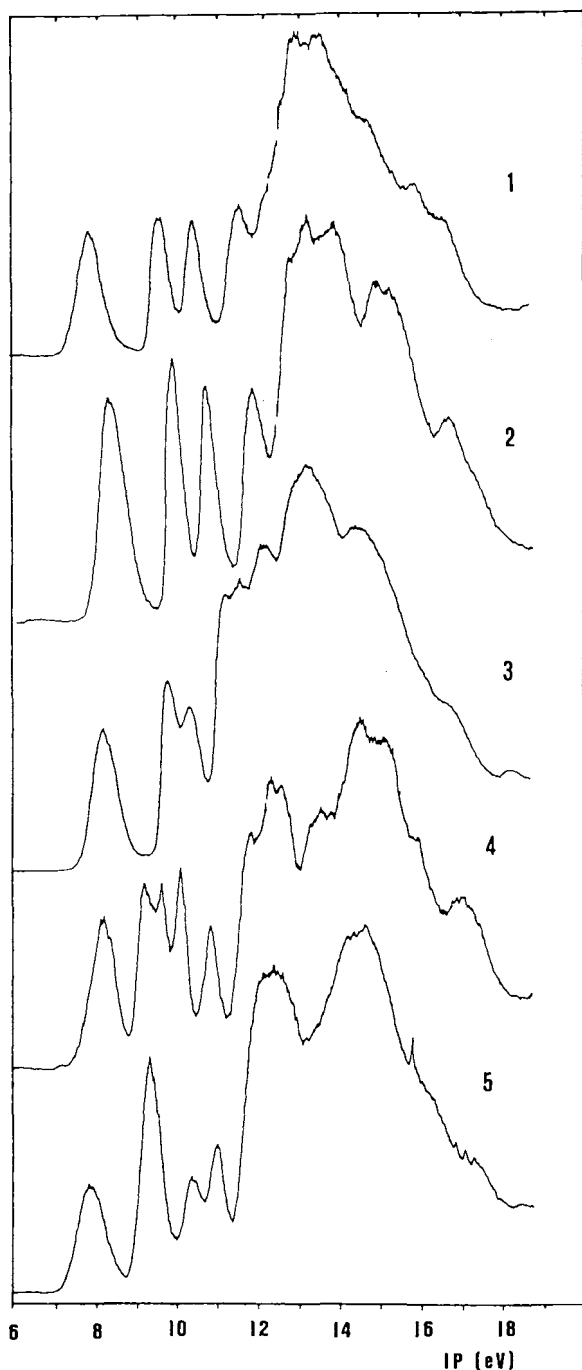
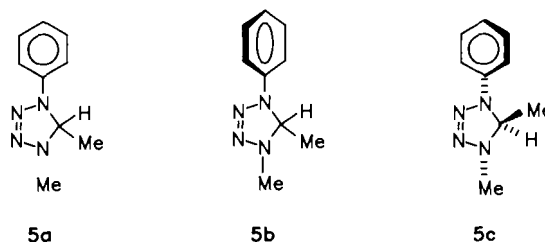


Figure 1. PE spectra of tetrazolines **1–5**



We have performed MNDO<sup>10)</sup> and AM1<sup>12)</sup> calculations with complete geometry optimization for these two conformers. The results are summarized in Table 3. From these data no definite statement concerning the relative stabilities of **5a** and **5b** is possible. Due to different parameterization of the two semiempirical methods the absolute values of  $\Delta H_f$  vary strongly for MNDO and AM1, but results concerning relative thermodynamic stabilities of conformers should be significant from both methods. The data show a difference in the stabilities of **5a** and **5b** in the order of 4–10 kJ/mol indicating a rather low rotational barrier for the phenyl group. However, according to MNDO, **5b** should be the preferred conformer while AM1 favours **5a**. Since the AM1 method can be considered as superior to MNDO in the investigation of compounds like **5**, the latter result should be favored.

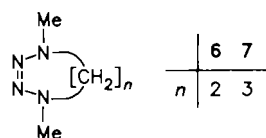
In certain cases it has been possible to derive further arguments for conformational analysis when calculated orbital energies are correlated with observed IPs<sup>13)</sup>. However, due to the approximative nature of the Koopmans theorem<sup>8)</sup> no definite result can be expected by this way<sup>14)</sup>. As is apparent from the data given in Table 3, calculated orbital energies correlate slightly better with IPs for **5a** than for **5b**. This is a further argument in favor of **5a**.

According to the AM1 results, in the most stable conformation (**5c**) the phenyl group is slightly rotated [ $\Phi(\text{N–N–C–C}) = -23^\circ$ ] against the essentially planar

tetrazoline ring. The exactly coplanar conformation **5a** ( $\Phi = 0^\circ$ ) is about 2 kJ/mol less stable than the former one indicating a very low barrier for torsional movement. In **5c** both amino nitrogen atoms have pyramidal configurations; their substituents are on the same side of the tetrazoline ring, opposed to the C-methyl group.

According to AM1 the  $\pi$ MOs of the phenyl group remain unshifted when the torsional angle  $\Phi$  is varied while in MNDO the split of these orbitals is conformation-dependent. The observed single ionization band for  $\pi(\text{Ph})$  (see above) is in agreement with the AM1 results.

Previously it has been shown that thermal stabilities of 2-tetrazenes are related to the energy difference  $\Delta IP$  of  $\pi_2$  and  $\pi_3$ <sup>51</sup>. For cyclic 2-tetrazenes a remarkable variation is found with ring size which is reflected in the  $\Delta IP$  values: In the rather instable seven-ring 2-tetrazene **7**  $\Delta IP$  is only 0.11 eV, while in the more stable six-ring homolog **6**  $\Delta IP$  is equal to 0.85 eV<sup>51</sup>.



Compared with **6** and **7**, the five-membered ring compounds **1–5** are rather stable towards thermal decomposition<sup>41</sup>. This is consistent with a large  $\Delta IP$  of 1.6–1.8 eV of **1–4**. In compound **5**  $\Delta IP$  is further increased due to asymmetric substitution of the 2-tetrazene unit. As has been shown, the “ $\Delta IP$ /stability” rule is related to the different bonding properties of  $\pi_2$  and  $\pi_3$ <sup>15</sup>.  $\pi_2$  is N–N bonding and N=N antibonding, whereas  $\pi_3$  is N–N antibonding and N=N bonding. Thus, stabilization of  $\pi_2$  and destabilization of  $\pi_3$  will strengthen the N–N bond. Furthermore, there is an inverse linear correlation ( $r = 0.998$ ) between  $\Delta\pi$  and the bond order of the N=N bond.

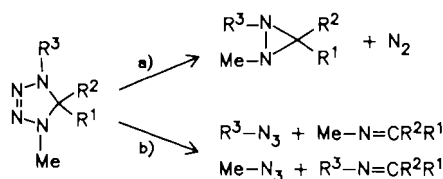
### Thermolysis of Tetrazolines 1–5

For thermolysis of 2-tetrazolines two decomposition paths are observed<sup>41</sup>:

(a) Ring contraction leading to diaziridines.

(b) Cycloreversion yielding imines and azides.

Solution studies in  $[\text{D}_8]$ toluene at 100°C revealed path b) usually to be the preferred reaction, but in certain cases, depending on the substituents, also diaziridines are formed<sup>41</sup>.



We have studied the pyrolysis of compounds **1–5** in the gas phase by photoelectron spectroscopy at elevated temperatures<sup>6,7</sup>. The decomposition products were easily identified by their ionization potentials. As an example, Figure 2 represents the PE spectrum of tetrazoline **3** re-

corded at 370°C. The bands of **3** (Figure 1) have disappeared and the products, *N*-methylneopentanimine and methyl azide<sup>16</sup>, are detected from their strong ionization bands at

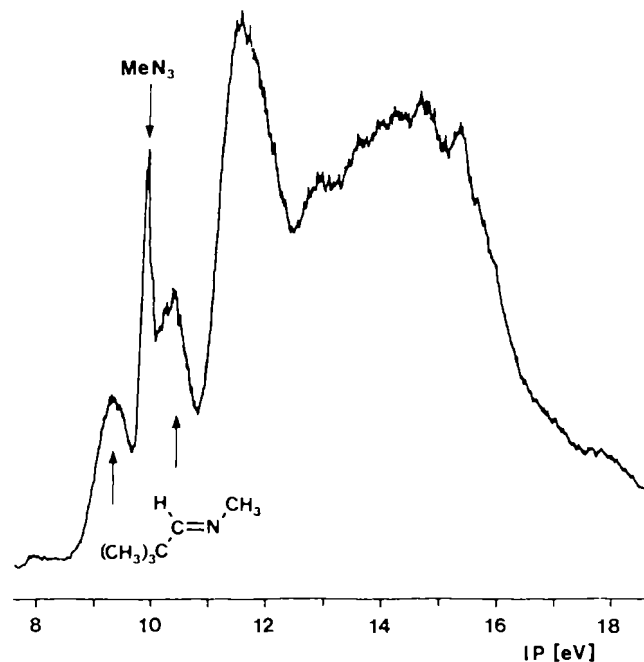


Figure 2. PE spectrum of tetrazoline **3** recorded at 370°C indicating decomposition products *N*-methylneopentanimine and methyl azide

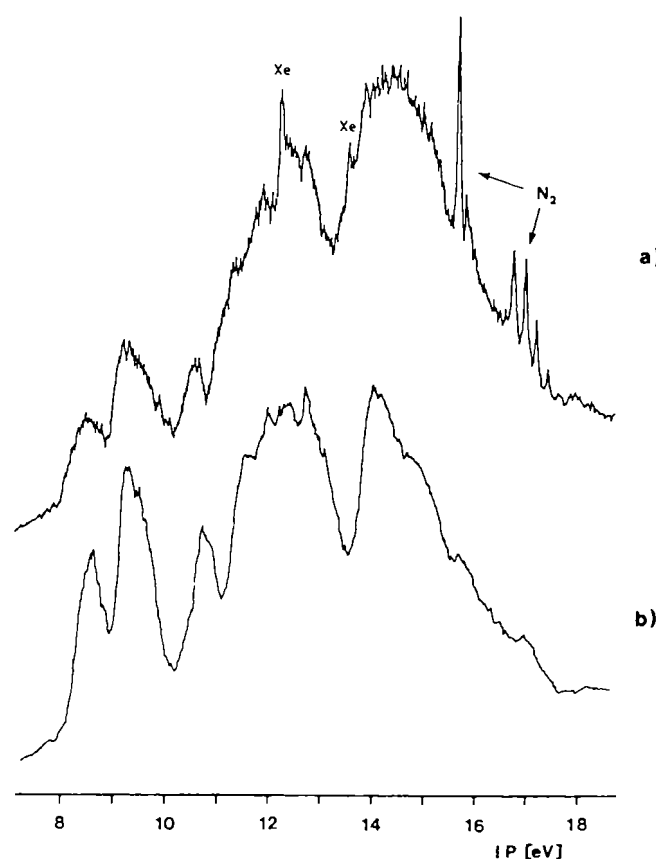


Figure 3. PE spectrum of tetrazoline **5** recorded at 370°C (a) indicating decomposition products diaziridine **10** and nitrogen. PE spectrum of **10** recorded at 22°C (b)

9.31 and 10.35 eV and at 9.82 and 11.32 eV, respectively. Similarly, in Figure 3 the peaks of tetrazoline **5** have disappeared and instead of them ionization bands of molecular nitrogen and 1,3-dimethyl-2-phenyldiaziridine (**10**) are discernible. The results for tetrazolines **1–5** are summarized in Table 4; the relevant ionization potentials of all products are collected in Tables 5 and 6.

Table 4. Products of thermal gas-phase decomposition of tetrazolines **1–5**

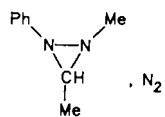
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	No.	Temp. [°C]	Route	Products
Me	Me	Me	1	400	b)	Me <sub>2</sub> C=NMe, Me-N <sub>3</sub>
H	Me	Me	2	400	b)	MeCH=NMe, Me-N <sub>3</sub>
H	<i>t</i> Bu	Me	3	370	b)	<i>t</i> Bu-CH=N-Me, Me-N <sub>3</sub>
H	Ph	Me	4	375	b)	Ph-CH=N-Me, Me-N <sub>3</sub>
H	Me	Ph	5	370	a)	

Table 5. Vertical ionization potentials [eV] of imines R<sup>1</sup>R<sup>2</sup>C=N-Me

R <sup>1</sup>	R <sup>2</sup>	n	π	π(Ph)	Ref.
Me	Me	9.10	10.2		16,17)
H	Me	9.50	10.67		
H	<i>t</i> Bu	9.31	10.35		
H	Ph	8.80	10.85	9.38	

Table 6. Vertical ionization potentials *IP* [eV] and orbital energies  $\epsilon$  [eV] of 1,3-dimethyl-2-phenyldiaziridine (**10**)

<i>IP</i>	$-\epsilon^a)$	Assignment
8.52	9.02	$\pi(\text{Ph}), n_{\text{N}}$
9.22	9.41	$\pi(\text{Ph})$
9.6	10.57	$n_{\text{N}}^{\uparrow}$
10.72	11.62	$n_{\text{N}}^{\downarrow}$

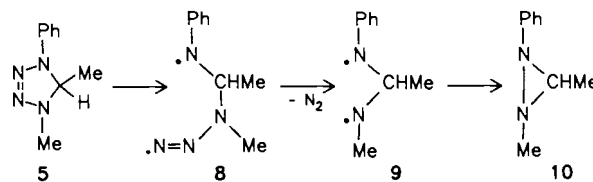
<sup>a)</sup> MNDO results.

PE spectra of several imines have already been studied<sup>16,17)</sup> and the variation of IPs with substitution is well understood. Therefore, identification of these compounds and assignments of IPs to molecular orbitals (Table 5) are quite unequivocal. Analysis of the PE spectrum of diaziridine **10** is based on MNDO calculations (Table 6) and comparison with the spectrum of 1,2-dimethyldiaziridine<sup>18)</sup>.

In some cases also secondary decomposition products are observed. For example, methyl azide is split to molecular nitrogen and methanimine. These compounds are also identified from their known PE spectra<sup>16,17)</sup>.

The divergent pyrolytic reaction of tetrazoline **5** certainly has to be associated with the *N*-phenyl group of this com-

pound. It is well-known that tetraaryl-2-tetrazenes are considerably less stable than the corresponding alkyl compounds<sup>19)</sup>. Accordingly, the two NN single bonds in **5** can be expected to differ in strength. While for **1–4** a concerted mechanism can be anticipated for cycloreversion, a stepwise radical decomposition seems to be likely in the case of **5**. The initial step probably is the scission of the N–N bond between the *N*-phenyl and the azo group. Homolysis of this N–N bond will be favored through stabilization of the aminyl radical by the phenyl group. The resulting 1,5-diradical **8** easily would lose molecular nitrogen<sup>20)</sup> leading to a 1,3-diradical **9** that would recombine to give the diaziridine **10**. A similar stepwise mechanism has been discussed by Gowenlock et al.<sup>21)</sup> for decomposition of acyclic 2-tetrazenes. It has however to be stated that until now we have no experimental evidence supporting the proposed mechanism. In particular, it was not possible to detect the intermediates **8** and **9** in the PE spectrum during pyrolysis.



## Conclusion

In the gas phase, aliphatic tetrazolines thermally are cleaved by cycloreversion to imines and azides. Ring contraction to diaziridines is only likely to occur for tetrazolines with aromatic *N*-substituents or other groups stabilizing aminyl radicals.

We are indebted to Prof. Dr. E.-U. Würthwein, Münster, for performing the AM1 calculations.

## Experimental

PE spectra were recorded on an UPG 200 spectrometer of Leybold-Heraeus equipped with a He(I) lamp (21.21 eV) as radiation source. The spectra were calibrated with the lines of Xenon at 12.130 and 13.436 eV and of Argon at 15.759 and 15.937 eV. The accuracy of the measurements is approx.  $\pm 0.03$  eV for ionization potentials, for broad or overlapping signals it drops to  $\pm 0.05$  eV. Thermolysis is carried out in a tube of about 70-mm lengths and 4.5-mm inner diameter, which is placed between the sample inlet system and the ionization chamber. The distance between thermolysis tube and ionization chamber is about 100 mm. Temperatures are accurate to ca.  $\pm 5^\circ\text{C}$ .

The syntheses of tetrazolines **1–5** have been described elsewhere<sup>3,4)</sup>.

## CAS Registry Numbers

1: 113893-43-9 / 2: 97325-69-4 / 3: 113893-44-0 / 4: 41217-39-4 / 5: 41217-46-3 / 8: 113893-45-1 / 9: 113893-46-2 / 10: 51456-64-5 / MeN<sub>3</sub>: 624-90-8 / Me<sub>2</sub>C=NMe: 6407-34-7 / MeCH=NMe: 6898-67-5 / *t*BuCH=NMe: 26029-56-1 / PhCH=NMe: 622-29-7

<sup>1)</sup> See e. g.: F. R. Benson, *The High Nitrogen Compounds*, Wiley, New York 1983.

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