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ELECTRONIC STRUCTURES AND THERMOLYSES OF 2-TETRAZENES

Peter Heymanns and Paul Rademacher*

Institute of Organic Chemistry

University of Essen

Universitaetsstr. 5, D-4300 Essen 1 (W. Germany)

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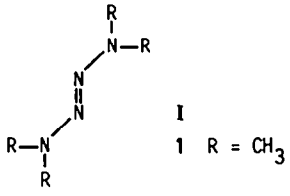
Abstract - The electronic structures and gas phase thermolyses of the cyclic 2-tetrazenes **2** and **3** and of open chain 1,1,4,4-tetramethyl-2-tetrazene (**1**) have been studied by photoelectron spectroscopy. While the six-membered ring compound **2** yields 1-methylmethylenamine (**6**) and nitrogen as fragments, the seven-membered ring compound **3** is contracted to 1,2-dimethylpyrazolidine (**11**). The acyclic 2-tetrazene **1** prefers disproportionation to **6** and dimethylamine (**7**). Based on MNDO calculations the ionization potentials of **1** - **3** were assigned to molecular orbitals. Several conformations of **2** and **3** were calculated. Compound **2** shows a rigid boat conformation with equatorial methyl groups, while **3** can occupy several conformations of similiar energies. The different thermal decompositions of **1** - **3** are explained.

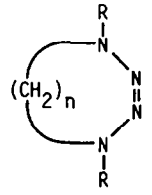
Introduction

Acyclic 2-tetrazenes I occupying a planar trans configuration were first described by E. Fischer[1] in 1879 and are easily accessible by oxidation of 1,1-disubstituted hydrazines[2]. In contrast to this, analogous cyclic compounds bearing a cis-tetrazene fragment II are much more difficult to prepare and until now only known as five-[3], six-[4] and seven-membered[5] ring compounds.



I

1 R = CH_3



II

2 R = CH_3, n = 2

3 R = CH_3, n = 3

Nitrogen extrusion from 2-tetrazenes I primarily yields aminyl radicals recombining to hydrazines or disproportionating to imines and amines[6]. The thermal stabilities of the cyclic compounds II vary with their ring size. Variable temperature photoelectron (PE) spectroscopy[7] has proved valuable in studying gas phase reactions[8]. Our PE spectroscopic studies were intended to examine the gas phase thermolyses of the methyl derivates **1** - **3**. All intermediates and products are of importance to analyse the decompositions. On the other hand, the different activation parameters (Table 1) should be elucidated.

Thermolyses of 1 - 3

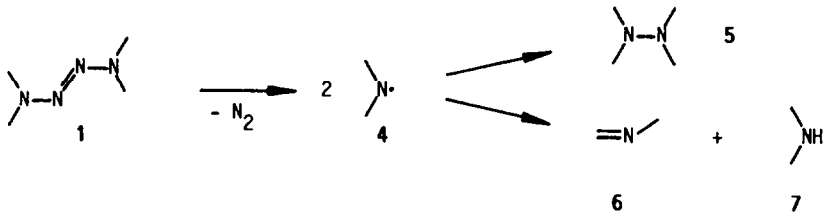
The activation parameters measured in solution for the methyl derivates **1** - **3**[4,5,9,10] are summarized in Table 1. The activation enthalpies and entropies of compounds **1** - **3** indicate great differences of their thermal stabilities. In particular, the relative low activation enthalpy and the negative activation entropy of **3** are noteworthy.

Gas phase thermolysis of 1,1,4,4-tetramethyl-2-tetrazene (**1**) yields dimethylaminyl radicals (**4**) and nitrogen. The radicals either combine to tetramethylhydrazine (**5**) or undergo disproportionation to 1-methylmethanimine (**6**) and dimethylamine (**7**)[6]. Kinetic investigations indicate that both N-N bonds of **1** are split simultaneously rather than stepwise[9].

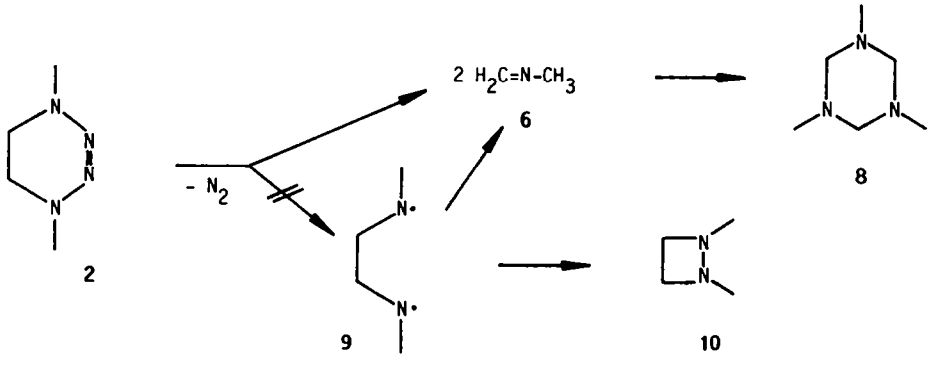
Table 1. Activation parameters for the thermolysis of compounds 1 - 3.

Compound	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/K mol)
1	151[a], 188[b]	19.7[a]
2[c]	159	71.2
3[d]	78.7	-84.6

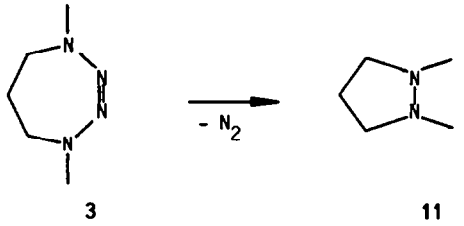
a) Ref. 9; b) Ref. 10; c) Ref. 4; d) Ref. 5.



The thermally[11] or photochemically[4] induced fragmentation of 1,3-dimethyl-1,4,5,6-tetrahydro--1,2,3,4-tetrazine (2) leads to 6 which trimerizes to 1,3,5-trimethylhexahydro-1,3,5-triazine (8). Nelsen et al.[4] proposed the biradical 9 to be an intermediate, but that was not in accord with results of Seebach et al.[11] who found no N,N-dimethyl-1,2-diazetidine (10), and thus the appearence of 9 seems to be unlikely. They proposed the reaction to be a [2+2+2]cycloreversion.



The pyrolysis of 1,4-dimethyl-1,4,5,6,7-pentahydro-1,2,3,4-tetrazepine (3) in solution (n-hexadecane) was investigated by Michejda et al.[5] 1,2-dimethylpyrazolidine (11) and nitrogen were the only products being detected. The negative activation entropy (see Table 1) leads to the conclusion that the transition state is educt-like and nitrogen extrusion does not occur in the rate-limiting step. In contrast to the radical mechanism found in the case of acyclic tetrazenes, a concerted process must be favoured. Furthermore, a conformational change is likely to happen before decomposition starts.



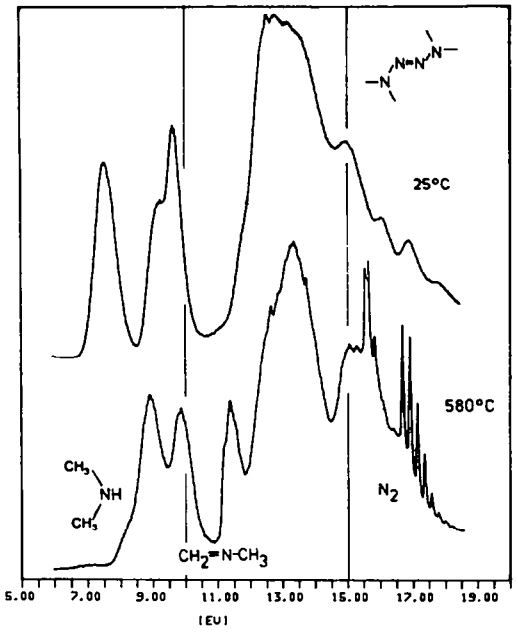


Figure 1. PE spectrum of 1 at 25 °C and at 580 °C.

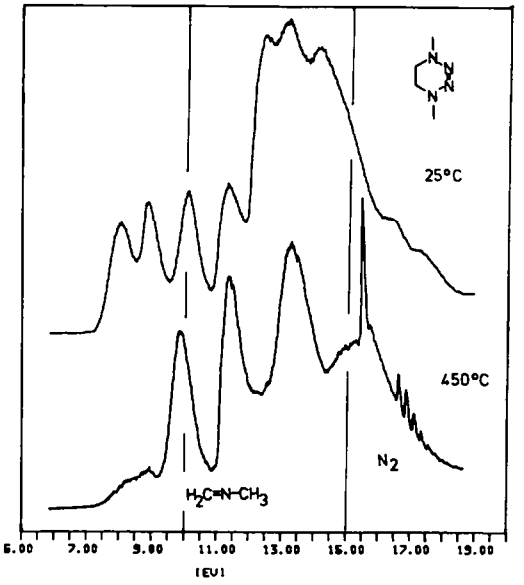


Figure 2. PE spectrum of 2 at 25 °C and at 450 °C.

Thermolyses of 1 - 3 Studied by Photoelectron Spectroscopy

PE spectra were recorded at room temperature and under conditions favouring thermolysis[7,8]. Spectral changes were detected during heating up. The bands of **1** at 7.66 (π_3), 9.38 (n_+), 9.78 (π_2) and 11.9 eV (Figure 1) decrease in intensity while the temperature is raised. The products **6** and **7** give rise to the bands at 9.90, 11.38 and 13.36 eV (**6**) and at 8.90 and 12.66 eV (**7**), respectively. Simultaneously the signals due to nitrogen (15.58 and 16.69 eV) increase. The shoulder at 8.2 eV can be assigned to a small amount of 1,3,5-trimethylhexahydro-1,3,5-triazine (**8**)[12], the trimer of **6**.

Heating to 450 °C leads to a decrease in the intensities of the ionization bands of **2** at 8.11 (π_3), 8.96 (π_2), 10.21 (n_-) and 11.44 eV (n_+) (Figure 2). Simultaneously the bands due to **6** at 9.90, 11.38 and 13.36 eV become stronger. Since other products could not be detected, the molecule is subject to a symmetrical bond cleavage yielding **6** and nitrogen. **6** can also be obtained by gas phase pyrolysis of **8**[13]. The high-temperature spectrum of **2** shows no signals that could originate from **8**.

The PE spectrum of **3**, recorded at 20 °C, exhibits signals of minor intensity due to 1,2-dimethylpyrazolidine (**11**)[14] (Figure 3), indicating **3** being instable already at room temperature. At 310 °C the starting material has disappeared completely and only bands arising from **11** and nitrogen are observed. **3** exhibits two overlapping signals of equal intensity at 8.44 (π_3) and 8.55 eV (π_2) and additional bands at 10.27 (n_-) and 11.70 eV (n_+). **11** is known to populate several conformations, the signals at 7.78 and 10.02 eV are due to the prevailing envelope conformation, the weaker bands at 8.3 and 9.0 eV arise from the half-chair conformation[14]. In the high-temperature spectrum of **3** no indications of further products are found.

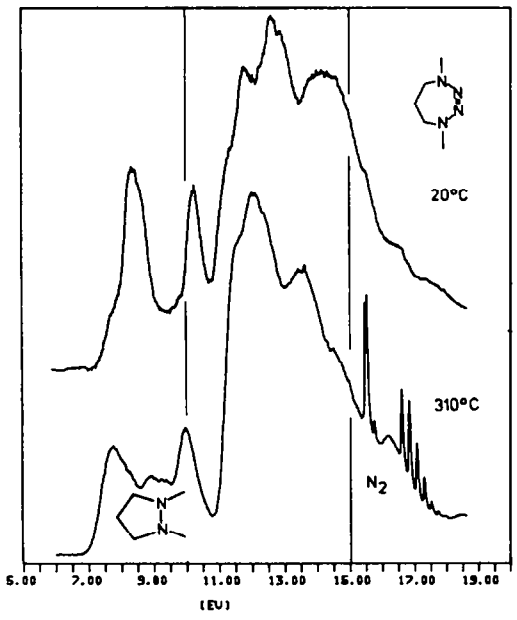
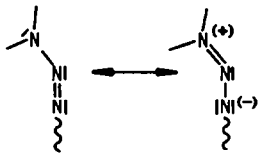


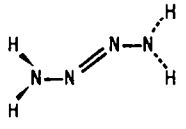
Figure 3. PE spectrum of **3** at 20 °C and at 310 °C.

The thermolyses of the compounds **1** - **3** differ in the following respects: the acyclic 2-tetrazene **1** undergoes disproportionation in the gas phase after nitrogen extrusion, which leads to **6** and **7**. The cyclic tetrazene **2** is cleaved symmetrically to **6** and nitrogen, while **3** undergoes ring contraction to **11**. In solution, **1** shows a preferred dimerization of the aminyl radicals **4** yielding tetramethylhydrazine (**5**)[9], from **2** the trimer of **6** is formed[4,11], while for **3** the same ring contraction as in the gas phase is observed[5].

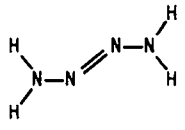
Electronic Structures, Conformational Properties and Stabilities of 1 - 3

The interactions of π- and n-orbitals in the tetrazene group have different effects on the thermal stabilities of the acyclic trans- and the cyclic cis-tetrazenes. Between the electron lone-pairs of the amino nitrogen atoms and the central azo group conjugation is possible.





12a

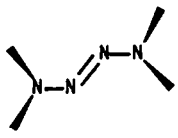


12b

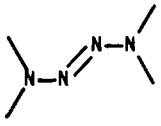
The low rotational barrier of the N^1-N^2 and the N^3-N^4 bond indicates that this conjugation is only of minor importance in the case of compound **1**[15]. Wiberg et al.[16] studied the PE spectrum of unsubstituted 2-tetrazene (**12**). Their assignments, which are based on CNDO/S calculations, correspond with our MNDO results. According to this, **12** has a structure with C_i symmetry **12a** in which the amino nitrogens are pyramidal. A planar C_{2h} structure **12b** is less stable than **12a** by 50.5 kJ/mol.

By vibrational spectroscopy it was shown that the most stable conformation of **1** is centrosymmetric (C_{2h} symmetry)[6]. In addition to this a trace of a second conformer of lower symmetry (C_1 or C_2) has been found. In the PE spectrum of **1**, formerly inspected by Gleiter and coworkers[17], only one conformer is detected.

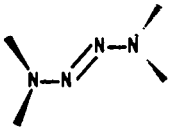
For the planar conformation **1b** and conformers with flattened pyramidal amino nitrogen atoms (**1a** and **1c**) essentially equal heats of formation are calculated by the MNDO method (Table 2). Structures with twisted dimethylamino groups like **1d** are less stable by 6 - 9 kJ/mol. This result is in accord with the low rotational barrier found for **1**[15]. Since for **1a** - **1c** no significant differences in the electronic structure are to be expected, a distinction based on the PE spectrum would be rather difficult.



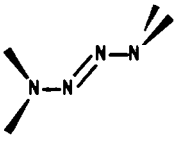
1a



1b

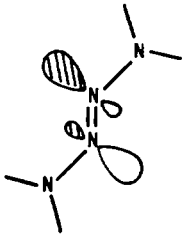


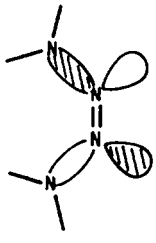
1c



1d

Cyclic tetrazenes II, fixed in a cis configuration, facilitate strong n/π-conjugation. With respect to the thermolyses of cyclic and acyclic 2-tetrazenes it is important to notice that the interactions of the n-orbitals are dependent on configuration. While in the trans form the mutual interaction of the n-orbitals on N^2 and N^3 is dominating, in the cis form their interaction with the vicinal N-N single bonds is favoured. By the latter type of interaction the N^1-N^2 and the N^3-N^4 bonds are weakened, thus easing their cleavage.





MNDO calculations have been performed for several conformations[18] of **2** and **3**. The results are summarized in Table 2. The half-chair conformation **2a** (C_2 symmetry) differs only slightly in its heat of formation from the boat conformation **2b** (C_s symmetry). Both methyl groups are in equatorial positions (ee). The ae conformers **2c** and **2d** are about 95 - 110 kJ/mol less stable than **2a** and **2b**. Of the various conformations of **2** the calculated orbital energies (π_3, π_2, n_-, n_+) of **2b** show the best agreement with the experimental ionization potentials.

2a

2b

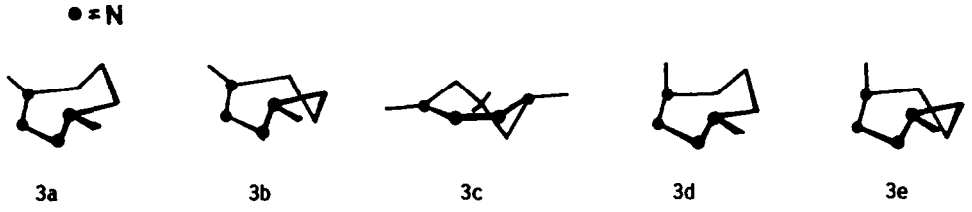
2c

2d

For 1,4-dimethyl-1,4,5,6,7-pentahydro-1,2,3,4-tetrazepine (**3**) calculations were performed on the chair (**3a**), boat (**3b**) and the twist-boat conformation (**3c**) with diequatorial methyl groups. In addition a chair (**3d**) and a boat form (**3e**) with equatorial-axial (ea) methyl groups were investigated. **3a**, **3b** and **3c** are of comparable energies whereas **3e** and **3d** are 50 and 95 kJ/mol, respectively, less stable. The best correlation between ionization potentials and orbital energies is found for **3a**. Diequatorial positions of the methyl groups in the cyclic compounds **2** and **3** are also in accord with dynamic NMR investigations[4,19].

Table 2. Heat of formation ΔH_f (kJ/mol) for several conformations of 1 - 3 (MNDO results).

Conformation		ΔH_f (kJ/mol)
1a	(C_2)	208
1b	(C_{2h})	211
1c	(C_i)	210
1d	(C_1)	217
2a	(C_2)	183
2b	(C_s)	181
2c	(C_1)	290
2d	(C_1)	275
3a	(C_s)	199
3b	(C_s)	209
3c	(C_2)	199
3d	(C_1)	295
3e	(C_1)	258



3a 3b 3c 3d 3e

In Figure 4 a correlation diagram is shown for the n- and π-MO's of 1 - 3 based on the observed ionization potentials.

For the split ΔIP of the two n-orbitals of the azo group, which corresponds to the energy difference of the linear combinations n_+ and n_-, the following values have been found:

$\Delta IP(1) = 3.50$ eV[20]
$\Delta IP(2) = 1.23$ eV
$\Delta IP(3) = 1.24$ eV

For the two cyclic compounds 2 and 3 the ΔIP values as well as the MO energies are essentially the same. In contrast to this, the acyclic molecule 1 shows a much greater split, which can be explained by a larger overlap of the n orbitals on N^2 and N^3 in the trans configuration. Apart from this, it is noteworthy that the n-ionizations of 1 - 3 have the same average value, $(n_- + n_+)/2$, which is close to 10.9 eV. This supports our assignments of the ionization potentials.

The energy of the π_2-orbital increases in the sequence 1, 2 and 3. This is equivalent to a destabilization of the N^1-N^2 and the N^3-N^4 bond and as a consequence the activation enthalpy for nitrogen extrusion is lowered. On the other hand, π_3 is stabilized in the same order. By this the N=N bond is strengthened and extrusion of nitrogen is favoured. This electronic behaviour might

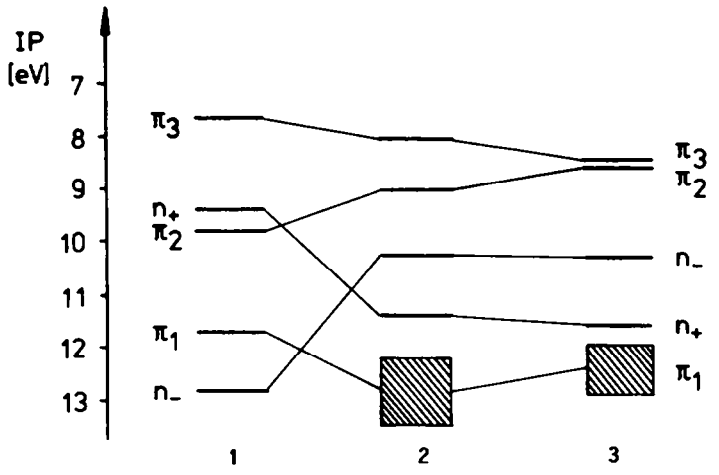


Figure 4. Correlation diagram for **1** - **3**.

have strong consequences for the thermal stability of tetrazenes. The activation parameters for the thermolysis of **1** - **3** (Table 1) reveal decreasing stability going from compound **1** over **2** to **3**.

Due to MNDO calculations compound **3** occupies three conformations of similar energies with equatorial methyl groups (**3a**, **3b**, **3c**). This makes the molecule likely to be rather flexible. Conformation **3e** bearing an axial methyl group is 60 kJ/mol less stable. The decomposition of **3** propably occurs from this rigid conformation. The relative low activation enthalpy and the negative activation entropy are in accord with these ideas.

In contrast to **3** the structure of **2** is probably more rigid, since the most stable conformers (**2a** and **2b**) differ only slightly in structure. The energy difference to the ea conformations **2c** and **2d** is much greater than in the case of **3**. In the ea conformations the 2-tetrazene unit is destabilized since the lone-pair of one amino group is moved out of conjugation with the NN double bond. Now this equatorial lone-pair is antiperiplanar to the C-C bond, which is weakened by n/σ^* interaction facilitating its cleavage during the fragmentation of **2**.

Conclusion

The striking differences in the thermolyses of compounds **1** - **3** have been investigated by PE spectroscopy. All decomposition products could be identified by their ionization potentials. MNDO results reveal that the six-membered ring compound **2** has a rigid structure while the seven-membered ring compound **3** is rather flexible. The fragmentations of **2** and **3** are probably initiated by a conformational transition of one methyl group into an axial position.

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Experimental

PE spectra were recorded on a 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. ± 0.03 eV for ionization potentials, for broad or overlapping signals it drops to ± 0.05 eV. Thermolysis is carried out in a tube of about 70 mm lenghts 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. ± 5 °C.

Tetramethyl-2-tetrazene (1) was prepared from dimethylamine by nitrosation, subsequent reduction to 1,2-dimethylhydrazine followed by oxidation[2,21,22]. 1,4-Dimethyl-1,4,5,6-tetrahydro--1,2,3,4-tetrazine (2) was obtained from dimethylnitrosamine and lithium-diisopropylamide as described by Seebach et al.[11] Oxidation of N,N'-dimethyl-N,N'-diamino-1,3-diaminopropane with potassiumhexacyanoferrate(III) yields 1,4-dimethyl-1,4,5,6,7-pentahydro-1,2,3,4-tetrazepine (3) according to Michejda et al.[5]

MNDO calculations[23] were carried out on an IBM 370 computer.

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