*Journal of Molecular Structure*, 175 (1988) 423–428
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

# ELECTRONIC STRUCTURES AND THERMOLYSES OF CYCLIC 2-TETRAZENES

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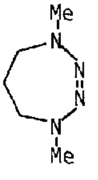
## ABSTRACT

The electronic structures of 2-tetrazenes **1** - **4** have been studied by UV photoelectron spectroscopy and MNDO calculations. Gas-phase thermolyses of these compounds were investigated by variable temperature PES. We found that the relative stabilities of cyclic 2-tetrazenes strongly depend on ring-size. The total bond order of the N=N bonds can be correlated with the energy differences of the respective first and second ionization potential.

## INTRODUCTION

2-Tetrazenes are compounds of variable stability with a four-nitrogen chain and a central NN double bond. Thermal decomposition of such molecules has been investigated by several authors (ref. 1). We have studied the electronic structures of cyclic 2-tetrazenes **1** - **3** by UV photoelectron spectroscopy and MNDO calculations and their gas-phase thermolyses by variable temperature PES (refs. 2,3). Acyclic 1,1,4,4-tetramethyl-2-tetrazene (**4**) was included for comparison. We found that the relative stabilities of 2-tetrazenes, which vary strongly with ring size, can be correlated with the energy differences of the respective first and second ionization potential.



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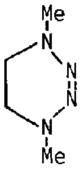

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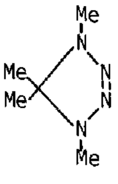

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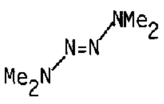

**4**

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## RESULTS

### PE-Spectra and Thermolyses of Compounds **1** - **4**

PE spectra of **1** - **4** (cf. refs. 4,5) have been obtained at ambient temperature and under conditions favouring thermolysis (ca. 300 - 700°C). Primary and secondary pyrolytic reaction products could be identified from their PE spectra. As an example, in Fig. 1 PE spectra of tetrazoline **3** recorded at 20, 400 and 660°C are depicted. The spectrum at 400°C indicates a mixture of methylazide ($MeN_3$) and imine ($Me_2C{=}NMe$) as primary decomposition products of **3**. At 660°C also secondary reaction products ($N_2$, HCN, $H_2C{=}NH$) are present (cf. ref. 6).

Thermolyses of 2-tetrazenes **1** - **4** show a remarkable variation with ring size: While the seven-membered ring compound **1** is contracted to 1,2-dimethylpyrazoli-

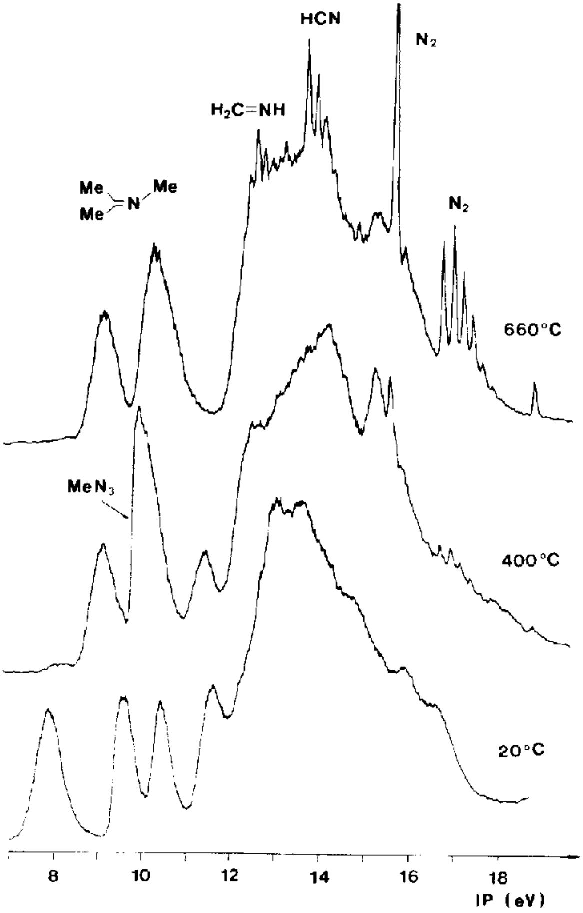
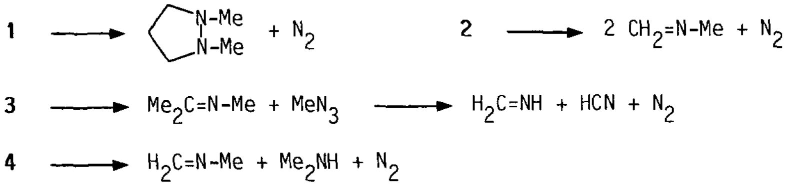


Fig. 1. PE spectra of compound 3 recorded at different temperatures.

dine (refs. 4,7), the six-membered homolog **2** is fragmented to $CH_2$=N-Me and $N_2$ (refs. 4,8), and the five-membered ring compound **3** suffers 1,3-dipolar cycloreversion to $MeN_3$ and imine (refs. 5,9). Acyclic 2-tetrazene **4** was found to disproportionate to imine and amine (refs. 1,4).



## Electronic Structures of Compounds 1 - 4

The electronic structure of 2-tetrazenes (refs. 4,5,10,11) is characterized by three occupied $\pi$-MO's ($\pi_1$ - $\pi_3$) and two n-type orbitals ($n_+$ and $n_-$) that are mainly localized on the nitrogen atoms of the azo group. Previous investigations have shown that in **1** - **3** orbital energies increase in the sequence $\pi_1$, $n_+$, $n_-$, $\pi_2$, $\pi_3$.. The MO's $\pi_2$ and $\pi_3$ of a cis-2-tetrazene unit, calculated by the MNDO method (ref. 12) for compound **2**, are depicted in Fig. 2. While $\pi_3$ is N=N bonding and N-N antibonding, $\pi_2$ has the opposite bonding properties. Thus, stabilization of $\pi_3$ and destabilization of $\pi_2$ rise the tendency of a 2-tetrazene for decomposition. This is in accordance with decreasing stability of cyclic 2-tetrazenes, when the ring-size is increased.

Fig. 2. MO's $\pi_2$ and $\pi_3$ of a cis-2-tetrazene.

In Fig. 3 a correlation diagram is shown for the ionization potentials of compounds **1** - **4** (refs. 4,5). Acyclic 1,1,4,4-tetramethyl-2-tetrazene (**4**) (refs. 4,8,11) has been included for comparison. It is evident from this diagram that the relative stabilities of these compounds towards thermal decomposition are proportional to the energy differences of the first two ionization potentials or, within Koopmans approximation (ref. 13), to the split $\Delta\pi$ of the highest two occupied MO's.

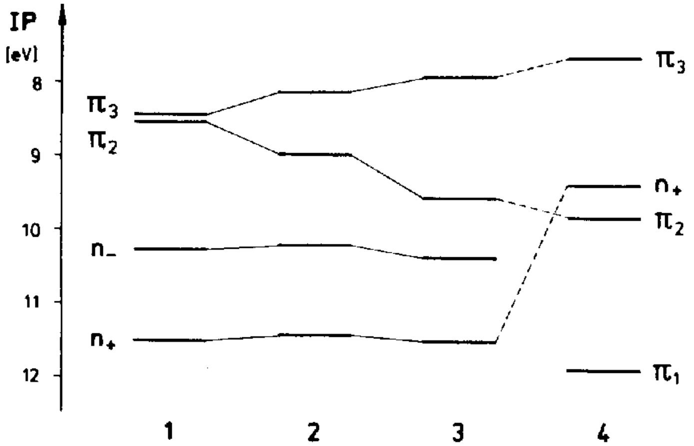


Fig. 3. Correlation diagram for ionization potentials of compounds **1** - **4**.

## Geometric Structures of Compounds **1** - **4**

For compounds **1** - **3** and for acyclic 1,1,4,4-tetramethyl-2-tetrazene (**4**) MNDO calculations have been performed (ref. 14). In table 1 the obtained N-N and N=N bond lengths r are summarized together with the corresponding total bond orders p.

TABLE 1
Bond lengths r (pm), bond angle $\alpha$ (°) and total bond orders (p) of compounds **1** - **4**.

| | r(N-N)[a] | r(N=N)[a] | $\alpha$(N=N-N)[a] | p(N-N)[b] | p(N=N)[b] |
|---|---|---|---|---|---|
| **1** | 136.4 | 122.1 | 126.0 | 1.35 | 2.20 |
| **2** | 135.2 | 123.0 | 122.1 | 1.42 | 2.10 |
| **3** | 136.0 | 123.9 | 112.2 | 1.37 | 2.01 |
| **4** | 134.8 | 124.7 | 116.4 | 1.45 | 1.93 |

[a] MNDO results.
[b] Calculted using Paulings formula r(p) = r(1) - k*logp (refs. 15,16).

These data correlate well with the tendency of **1** - **4** to decomposition. Compound **4**, which is the most stable one in this series, has the highest N-N and the lowest N=N bond order. On the opposite side, in the less stable molecule **1** elemental nitrogen is already preformed to a high degree (high N=N and low N-N bond orders).

## DISCUSSION

In Fig. 4 the $\Delta\pi$ values of **1** - **4** are plotted versus the respective N=N bond orders (table 1). The straight line with a correlation coefficient of 0.998 indicates that the strength of the N=N bond is determined by the energy difference of $\pi_3$ and $\pi_2$.

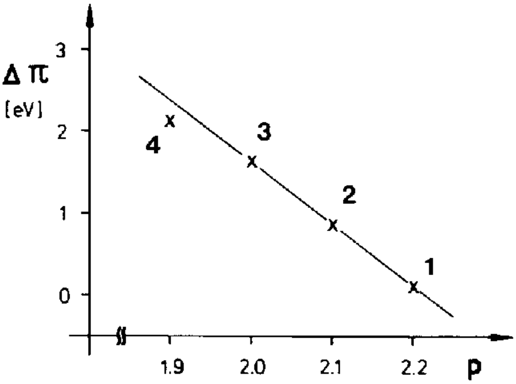


Fig. 4. Correlation diagram of energy difference $\Delta\pi$ and bond order p(N=N) of compounds **1** - **4**.

While in acyclic 2-tetrazenes like compound **4** $\Delta\pi$ is hardly affected by the alkyl substituents (ref. 14), in cyclic molecules (**1** - **3**) $\Delta\pi$ varies strongly with the ring size. Correspondingly, acyclic tetraalkyl-2-tetrazenes have very similar stabilities, whereas in cyclic 2-tetrazenes stability is reduced when the ring becomes larger. The main reason for the destabilization of the 2-tetrazene unit in the series of cyclic molecules is the increase of the N=N-N bond angles in the cyclic skeleton (table 1). This leads to a rehybridization of the azo-nitrogen atoms from $sp^2$ towards $sp^1$, so the azo group becomes more $N_2$-like.

## CONCLUSION

It can be concluded that in 2-tetrazenes there is evidence for a close correspondence between thermal stability, geometric and electronic structure.

## EXPERIMENTAL

Compounds **1** - **3** were synthesized as described elsewhere (refs. 4,9).

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.

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