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# HeI PHOTOELECTRON AND THEORETICAL STUDY OF THE GAS PHASE FLASH PYROLYSIS OF TETRAZOLE AND ANALYSIS OF $CN_2H_2$ ENERGY HYPERSURFACE ☆

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The flash thermolysis of tetrazole in vapour phase (1 Pa) is analyzed by HeI photoelectron spectroscopy and quantum calculations (MNDO, ab initio, CI). Experimentally the thermal decomposition of (1H or 2H) tetrazole gives cyanamide (preferentially) and diazomethane. The analysis of the potential energy hypersurface of $CN_2H_2$ system has enabled the study of the eight possible isomers and the determination of the saddle points between the minima. This study shows that the fact that cyanamide and diazomethane could be observed is due to their thermodynamic stability and the reactivity of different isomers. A lowest energy pathway between tetrazole and cyanamide and diazomethane is proposed.

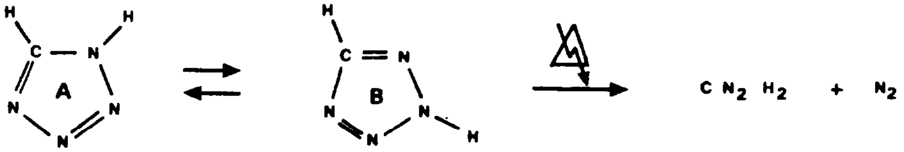
## 1. Introduction

In the context of a general study of the thermal decomposition of 5- and 6-membered heterocyclic compounds, we have experimentally and theoretically analyzed the flash thermolysis of tetrazole in the vapor phase. This compound exists in equilibrium between two forms (1H and 2H) and can lose a nitrogen molecule to form one or several products with the general formula $CN_2H_2$ (scheme 1).

This type of thermal expulsion of $N_2$ has been observed for similar compounds, such as 1,2,3-triazole or 1,2,3-thiadiazole, which yield acetonitrile [2] and thioketene [3], respectively.

We report data obtained by the use of an experimental setup coupling a flash thermolysis system with a photoelectron spectrometer, enabling the generated products to be characterized by determining their first ionization potentials. In the second part, these data are compared with theoretical results obtained by the analysis of the $CN_2H_2$ potential energy hypersurface. This was done with various semi-empirical (MNDO) and ab initio methods (see section 6). This hypersurface presents minima associated with stable or metastable isomers and saddle points connecting the different minima. There are eight of the latter as shown in scheme 2.

Three of these isomers are stable at low or ordinary



Scheme 1.

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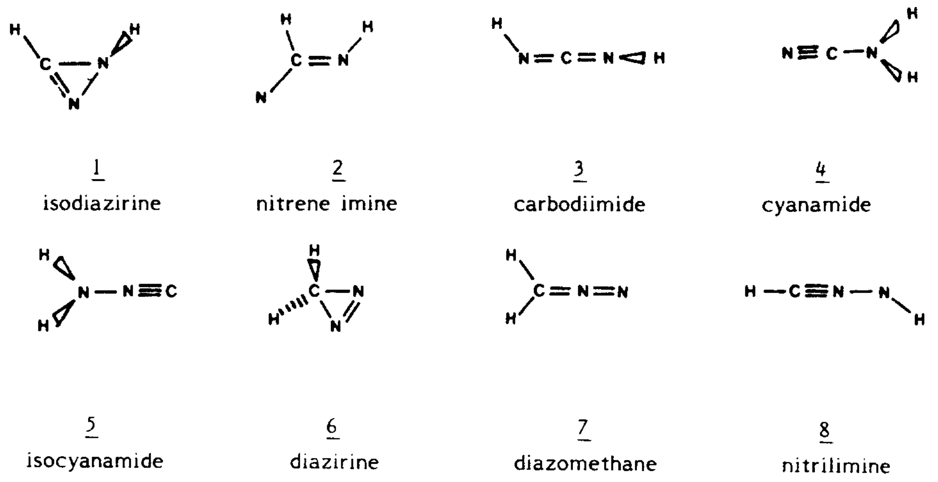
☆ Part 37 of "Applications of photoelectron spectroscopy to molecular properties", for part 36 see ref. [1].



Scheme 2.

temperatures, cyanamide **4**, diazirine **6** and diazomethane **7** [4–6]. In the case of carbodiimide **3** [5,7,8] and nitrilimine **8** [9,10], only the derivatives with large substituent groups have been isolated at ordinary temperature. The existence of isocyanamide in the vapor phase is controversial [5,7,11–14], even though its NMR spectrum has been obtained in solution [14]. Finally, isodiazirine **1** and a fortiori nitrene imine have never been observed.

## 2. Experimental results

The photoelectron spectrum of tetrazole (fig. 1), in agreement with Cradock and al. [15], presents three first bands (11.3, 12.1 and 13.7 eV) associated with five ionizations [16,17]. The first two bands overlap two different ionizations, corresponding to states $^2A''$ and $^2A'$. According to the calculations of Palmer and al. [17], these potentials are better described by the 2H structure (B).

The spectrum is totally modified above 1000 K (fig. 2), furnishing spectra characteristic of cyanamide **4** (fig. 3 and ref. [18]) and nitrogen (hatched bands in fig. 2). In addition, more total decomposition is shown by the appearance of cyanydric acid bands (also hatched in fig. 2). Furthermore, this spectrum shows another decomposition product associated with lower intensity bands at 9 and 15.2 eV. These bands can unambiguously be attributed to the spectrum of diazomethane **7**. The latter presents a third band at 14.1 eV [6] which is hidden in our spectrum by the fourth cyanamide band at 14.3 eV.

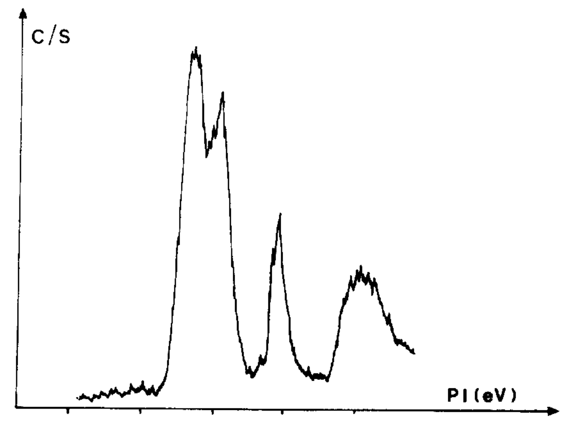


Fig. 1. HeI photoelectron spectrum of tetrazole before flash thermolysis.

It was of interest to compare these experimental attributions to the results of various ionization potential calculations done on compounds **3** to **8** (isomers **1** and **2** were eliminated since they are thermodynamically very unfavorable). Table 1 lists the potentials calculated with the MNDO and ab initio (3-21G* basis set) in the Koopmans approximation [19] ($IP \approx -\epsilon_i$), as well as after configuration interaction (CI). The table also lists published experi-

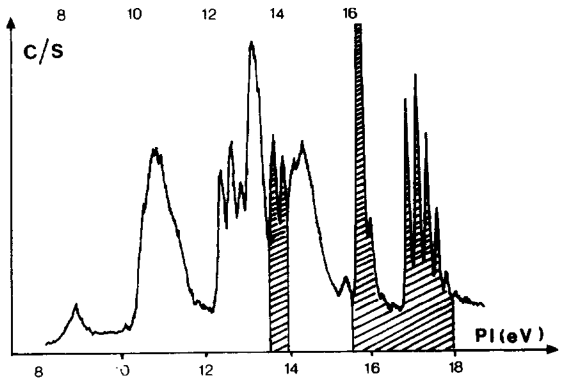


Fig. 2. HeI photoelectron spectrum of tetrazole after flash thermolysis (1100 K). The hatched bands correspond to HCN and $N_2$.

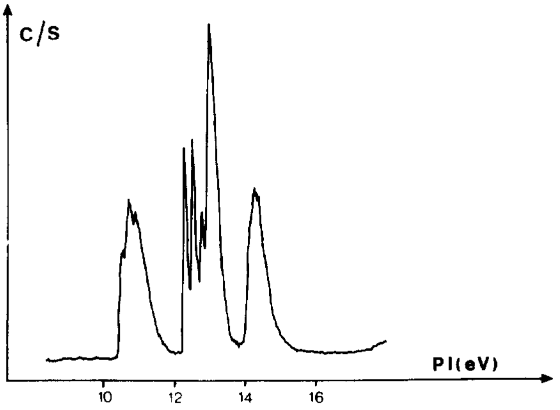


Fig. 3. HeI photoelectron spectrum of cyanamide.

mental potentials [6,18,20] and for the purpose of comparison the potentials calculated by Cambi et al. [21] using a method involving Green functions [22–24] in the case of compounds **4** to **7**.

The theoretical results are relatively satisfying with reference to the experimental data (compounds **4**, **6** and **7**), although they do not reach the quality of Cambi and al. Aside from cyanamide, they confirm that the attribution of experimental bands (9 and 15.2 eV) to diazomethane is the only possibility (the first potentials of **3**, **5** and **6** are too high). The only uncertainty at this level is the possible existence of nitrilimine **8**, the theoretical ionization potential of which is relatively close to those of diazomethane. It nevertheless seems necessary to eliminate this hypothesis on the basis of the results of Bock et al. [10] on $H_3C-C{=}N-N-Si(CH_3)_3$, whose first ionization potential was measured at 8.14 eV. It can be considered that the presence of methyl and trimethylsilyl groups decreases this potential by more than 1 eV (for this particular point the theoretical results in table 1 are mediocre, at least for the value of the first potential) which thus does not correspond to the experimental value of 9 eV.

## 3. Isomers of $CN_2H_2$

Before analyzing the different decomposition pathways of tetrazole, we present the results of calculations on $CN_2H_2$ isomers **1** to **8** which can be generated after this decomposition.

As a result of their small size, most of these molecules have been the object of a large number of theoretical studies [21,25–32]. They nevertheless remain partial, the most thorough being that of Moffat [28], who compared relative stabilities with an ab initio method (6-31G basis set). Similarly, with the exception of the cyanamide–isocyanamide equilibrium [30,31], no author has examined the other rearrangements.

Several calculation methods were used to explain the occasionally unusual structure of some of these isomers. Thus, in addition to the MNDO semi-empirical method previously used for tetrazole, molecular structures were optimized with the MONSTERGAUSS ab initio program on a 3-21G* basis set (d polarization orbitals on nitrogen). In addition, in order to estimate specific correlation effects, occasionally large in the case of rings [17], we carried out CI calculations on these optimized structures with the CIPSI method (see theoretical part).

Fig. 4 shows the ab initio geometric structures and table 2 lists the corresponding relative energy values (in relation to the most stable isomer, i.e. cyanamide **4**).

### *3.1. Isodiazirine 1*

Even though isodiazirine among all the isomers is the least stable after nitrene, it apparently plays a very special role, as will be seen in the study of thermal

Table 1
Experimental and calculated ionization potentials (eV) of the compounds 3 to 8

| Method | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|
| MNDO ($-\epsilon_i$) | 10.97 | 11.32 | 10.94 | 11.62 | 8.67 | 8.71 |
| | 11.44 | 13.09 | 12.72 | 12.95 | 13.42 | 10.91 |
| | 14.51 | 14.43 | 12.89 | 14.96 | 16.49 | 15.90 |
| | 15.12 | 15.11 | 15.18 | 17.11 | 16.75 | 16.01 |
| 3-21G* ($-\epsilon_i$) | 11.00 | 11.15 | 11.41 | 10.85 | 8.68 | 8.49 |
| | 11.18 | 12.58 | 12.19 | 13.03 | 14.27 | 10.64 |
| | 15.51 | 14.85 | 13.44 | 15.83 | 17.45 | 16.57 |
| | 15.78 | 15.45 | 16.28 | 18.11 | 18.00 | 16.60 |
| CI (IP) | 9.99 | 10.26 | 10.12 | 9.95 | 8.19 | 7.97 |
| | 10.11 | 12.30 | 10.44 | 13.06 | 13.82 | 9.80 |
| | 13.30 | 12.34 | 12.73 | 16.67 | 14.34 | 13.64 |
| | 13.47 | 13.67 | 14.81 | 15.07 | | 14.18 |
| exp. (IP) [a] | | 10.65 | | 10.75 | 9.00 | 8.14 [b] |
| | | 12.50 | | 13.25 | 14.13 | 8.69 [b] |
| | | 13.00 | | 14.15 | 15.13 | 10.30 [b] |
| | | 14.30 | | 17.50 | 16.93 | |
| Green fct. (IP) [c] | | 10.52 | 10.68 | 10.58 | 8.53 | |
| | | 12.41 | 10.85 | 12.98 | 14.18 | |
| | | 12.91 | 13.00 | 14.10 | 15.26 | |
| | | 14.30 | 15.41 | 17.51 | 17.33 | |

[a] Refs. [6,18,20]. [b] Value corresponds to $CH_3$-C-N-N-Si$(CH_3)_3$ [10]. [c] Ref. [21].

rearrangements. When only minimal ring motions are considered (ring opening and closure, 1–2 hydrogen migration), which in principle are the easiest, isodiazirine is a potential intermediate common to all the reactions except for cyanamide–isocyanamide isomerization.

In addition to pyramidalization of the amino nitrogen, the unusual N–N bond length should be remarked (1.56 Å) as should the already long C–N (H) bond (1.44 Å). These lengths can be correlated with the low stability of the molecule, corresponding to the particularly small Mulliken populations (0.14 for N–N and 0.18 for C–N, compared to 0.52 for C=N). These overlap populations reflect the weak nature of the N–N and C–N bonds, the rupture of which leads to preferential rearrangements.

### 3.2. Nitrene imine 2

Even though the most stable state of nitrenes is a triplet [33–36], it is admitted that the thermal decomposition of these compounds, the ground state of which is a singlet, preferentially yields one nitrogen molecule [37] and one nitrene [38,39], both singlets (spin conservation). The existence of nitrenes as metastable intermediates has very often been suggested in the degradation processes of nitrogen-containing molecules [38,40–43]. As in the case of vinyl nitrene [44] and 1,2,4-triazolo-3-nitrene [45], the lowest singlet state is not a closed shell state, but rather one of two open shells (corresponding to the most stable triplet), as shown by an MNDO calculation carried out with a CI limited to two frontier orbitals (this state is calculated to be 59 kJ mol$^{-1}$ lower than the ground singlet state with closed shells). This is confirmed by the ab initio CI calculation which accentuates the energy differences since it attributes to the two open shell singlet state an energy which is 98 kJ mol$^{-1}$ lower than that of the closed shell state (whereas it is 103 kJ mol$^{-1}$ higher than that of the corresponding triplet).

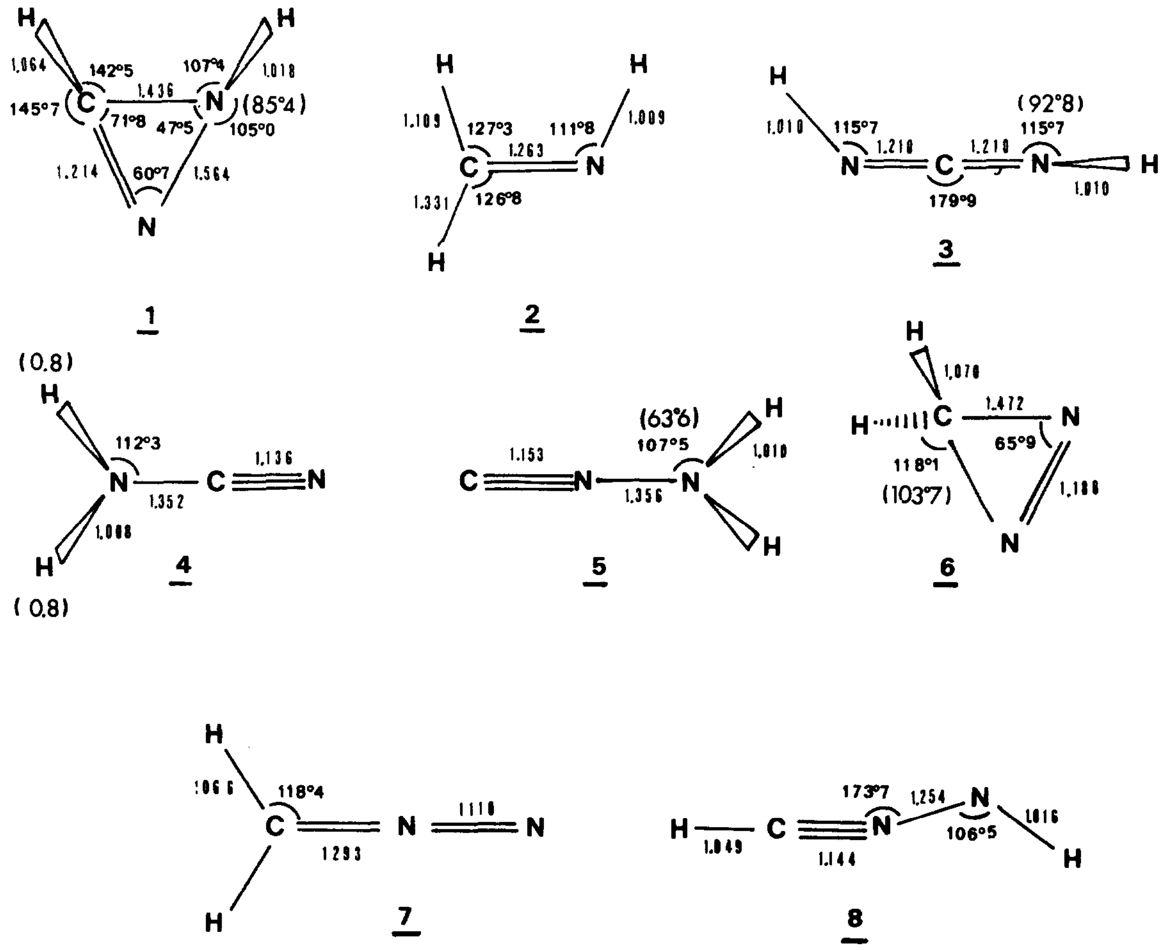


Fig. 4. Ab initio (3-21G*) structures of isomers 1 to 8. The values between parentheses are to diedral angles corresponding to the out-of-plane bonds.

Table 2
Relative total energies (kJ mol$^{-1}$) of the isomers 1 to 8 calculated at SCF level (MNDO and ab initio) and CI level. In the case of nitrene 2, the values between parentheses correspond to the closed shell state (see text)

| Method | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| MNDO | 232 | 318<br>(377) | 61 | 0 | 224 | 154 | 132 | 231 |
| 3.21G* (SCF) | 337 | (427) | 56 | 0 | 186 | 203 | 161 | 315 |
| 6.31G* (SCF) [a] | 414 | | 76 | 0 | 197 | 333 | 208 | 355 |
| CI | 296 | 395<br>(493) | 33 | 0 | 202 | 188 | 161 | 261 |

[a] Ref. [16].

### *3.3. Carbodiimide **3***

As was stated in section 1, nonsubstituted carbodiimide has never been isolated at ordinary temperature. It has, however, been identified by IR [46] at low temperature (argon matrix at 20 K). This is in apparent contradiction with the total energy value of this molecule, which is the most thermodynamically stable after cyanamide. This stability was confirmed by the fact that the compound was obtained from substituted tetrazoles [8]. The energy difference between carbodiimide and cyanamide is much lower (56 kJ $mol^{-1}$ at the SCF level and 33 kJ $mol^{-1}$ at the CI level) than that between ketenimine and acetonitrile (about 144 kJ $mol^{-1}$) [44,47]. The fact of its never having been observed is thus probably not due to its thermodynamic stability, but rather to its high reactivity [8,48,49]. This can be correlated with its electronic structure [50] and in particular with the polarization of the NCN system, reflected by greater net charges than those of the other isomers (table 3) and also greater than those calculated for its phosphorus homologues [51] (expected result when we consider the respective polarities of the C=N and C=P bonds).

The geometric structure of carbodiimide (fig. 4) is entirely comparable to that of homologous allene systems [51]: the NCN skeleton is practically linear ($\sigma$= 179.9°); the two HNC planes are practically orthogonal. These results are in perfect agreement with those of Nguyen and Hegarty [52], who among other things showed that the inversion barrier of nitrogen is very low (33 kJ $mol^{-1}$), in particular if it is compared to that of carbodiphosphine (176 kJ $mol^{-1}$) [51].

### *3.4. Cyanamide **4***

As a result of its high stability, cyanamide has been the object of a large number of studies. In fact, the first spectroscopic observations are almost 50 years old, with the beginning of systematic studies dating from 1958 [53]. Whether it be in the solid, liquid or vapor phase, it was shown that amino nitrogen was pyramidal [46,54–61] and that the inversion barrier was very low [62–65], subsequently confirmed by several calculations [31,32]. Our results (fig. 4) are thus in full agreement with published data, in particular with those of Ichikawa et al. [31], who examined the basic effects and those when polarization orbitals were taken into account, necessary for the nitrogen atoms. The absence of polarization orbitals yields a planar structure [66] [#1] as in the case of isocyanamide. On the other hand, their introduction gives a calculated structure (fig. 4) very close to the experimental structure [62].

### *3.5. Isocyanamide **5***

In parallel to cyanamide, isocyanamide has often interested theoreticians [18,19], since this isomerisation can be compared to that between acetonitrile and methyl isocyanamide [67–71] or between silanitrile and isosilanitrile [72–77]. Even though observed at low temperatures [78,79], isocyanamide is the least stable of these isomers, since it is calculated at more than 180 kJ $mol^{-1}$ higher than cyanamide (table 2), while methyl isocyanamide is only about 90 kJ $mol^{-1}$ higher than acetonitrile and methyl iso-

Table 3
Net charge (3-21G* calculations) of isomers **1** to **8**

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| C | 0.44 | 0.44 | 0.96 | 0.69 | 0.31 | −0.12 | −0.31 | 0.15 |
| N(H) | −0.59 | −0.75 | −0.83 | −0.90 | −0.53 | | | −0.53 |
| N | −0.46 | −0.24 | | −0.51 | −0.48 | −0.16 | −0.10, −0.07 | −0.30 |
| H(C) | 0.30 | 0.25 | | | | 0.22 | 0.24 | 0.39 |
| H(N) | 0.31 | 0.30 | 0.35 | 0.36 | 0.35 | | | 0.30 |

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[#1] In ref. [66] the MNDO calculations for **4** and **5** give false energy minima corresponding to a planar form. The true minima correspond to a pyramidal nitrogen and have an energy of 22.1 and 61 kJ $mol^{-1}$ lower, respectively.

silanitrile is more stable than methyl silanitrile (by 280 kJ $mol^{-1}$) [77]. This result agrees with the conclusions of Ichikawa et al. [31], as well as with our previous work [77] which has shown that the stability of this type of molecule can be correlated with the delocalization of the electron system and in particular with the overlap populations. The comparison of Mulliken populations confirms this hypothesis, since the bonds of **4** have a higher bonding character than those of **5**: 0.31 and 0.96 for $(H_2)N{-}C$ and $C{\equiv}N$ respectively in **4**; 0.25 and 0.50 for $(H_2)N{-}N$ and $C{\equiv}N$ in **5**. Finally, it should be noted that the polarization of **5** is much lower than that of **4** (table 3), consistent with its amine character (in comparison to the amide character of **4**), already mentioned by Ichikawa et al. [31].

### *3.6. Diazirine* **6**

Diazirine is one of the two stable isomers of $CN_2H_2$ and, as cyanamide, has been the object of numerous publications particularly on its thermal and photochemical stability [80]. The difference in energy between isomers **4** and **6** is comparable to that between 2H azirine and acetonitrile [44], which is nevertheless more difficult to isolate and which has been obtained by pyrolysis of vinyl azide [81–83] or of 1H-1,2,3-triazole [83] (catalytic reaction with $Cu_2O$). This suggests that the reactivity of **6** is lower than both its homologue azirine 2H and the other $CN_2H_2$ isomers. It is to be noted that the net charges of the principal atoms (C, N) are very low and are all negative, as in the case of diazomethane. In addition, the experimental stability and lower relative reactivity (compared to the other isomers) agree with the energies of the last occupied orbitals (see section 3.9).

### *3.7. Diazomethane* 7

Diazomethane is very important in organic chemistry as a result of its uses in 1–3 dipolar addition reactions [84]. From an energetic standpoint and although more stable, it is relatively close to isocyanamide **5** and diazirine **6**. This is not inconsistent with experimental data concerning heats of formation [85–87], which themselves are contradictory. Contrary to what the name 1–3 dipole may suggest, the net charges (table 3) remain low and comparable to that of its cyclic isomer **6**. Its reactivity is thus above all related to its energy position and to the form of its frontier orbitals [50,88,89].

### *3.8. Nitrilimine* **8**

Nonsubstituted nitrilimine has apparently not yet been observed [12], although several of its substituted derivatives have been characterized [10,90–93]. As for carbodiimide **3** and diazomethane **7**, nitrilimine is a synthon used in 1–3 dipolar additions to general five-membered heterocyclic compounds [84,94]. The ab initio calculated structure is consistent with that calculated in 6-31G basis set by Moffat [28] and corresponds to a relatively high energy, since it is close to its cyclic isomer isodiazirine **1**.

### *3.9. Comparative study of $CN_2H_2$*

As previously mentioned, semi-empirical MNDO calculations are very comparable to the more sophisticated ab initio calculations from a qualitative point of view. A single exception concerns the order of stability between isomers **5** and **6**. Configuration interaction calculations have shown that correlation effects are lower than expected, since the results after CI are very close to SCF results (table 2). If our results are compared to those of Moffat [28] (6-31G*), it is seen that, quantitatively, the basis effects are at least as important. Qualitatively and regardless of the calculation method, the stability order remains the same: **4**, **3**, **7**, **5**, **6**, **8** **1**, **2**. This order, however, does not correspond exactly to experimental observations, which give **4**, **6** and **7** as stable compounds, **5** being characterized with more difficulty and **3** never being observed. It may thus be concluded from this disagreement that the existence of these molecules in normal conditions can be correlated not only with their thermodynamic stability, but also with their reactivity. The latter is in general controlled by two types of factors: electronic charges (for highly polarized systems) and frontier molecular orbitals (in the case of more soft reagents) [95–99]. Thus, in the rapid description of the different isomers, we mentioned the very strong polarization of carbodiimide **3** (table 3) and, on the contrary, the very weak polarization of diazirine **6** and diazomethane 7. In the case of weak or moderate polarization, the energy and

Table 4
Eigenvalues $\epsilon_i$ (eV) in SCF (3-21G*) calculations associated with lowest unoccupied molecular orbital (LUMO) and with highest occupied molecular orbital (HOMO)

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| LUMO | 4.58 | 0.99 | 5.70 | 6.14 | 6.08 | 4.30 | 4.44 | 5.13 |
| HOMO | −10.47 | −10.02 | −11.00 | −11.07 | −11.17 | −10.74 | −8.57 | −8.49 |

form of frontier orbitals are very important. This was verified in particular in the case of 1–3 dipolar addition reactions with compounds such as carbodiimide **3**, diazomethane **7** and nitrilimine **8**. These compounds all have a π HOMO with out of phase orbitals on the terminal atoms, while the lowest vacant π type molecular orbital presents a node on each bond between the principal atoms. This orbital form is of fundamental importance in the case of cyclo additions, since it maximizes the stabilizing interactions which exist in transition states. This form of molecular orbital is not found in diazirine **6**, for which the HOMO is a σ type. In addition, the HOMO of this compound is much more stable than in **7** (table 4), which also contributes to its relative lack of reactivity.

Based on these remarks, it would seem that the thermodynamic order of stability should be corrected by a factor taking the reactivity of the different isomers into account. In particular, we may note the lower theoretical reactivity of diazirine in comparison to that of diazomethane (reactivity controlled by the frontier orbitals) as well as the high reactivity of carbodiimide (reactivity controlled by both frontier orbitals and charges).

## 4. Theoretical analysis of the thermal decomposition of tetrazole

### *4.1. 1H↔2H tetrazole equilibrium*

In solution, this equilibrium is very sensitive to the solvent and to the nature of substituents [100–102] and apparently favors the 1H form [103–105] (A). The same is true in solid state [106]. In the vapor phase, the conclusions are less clear cut [16,107,108] as shown by theoretical studies. At the SCF level, the energy of the 1H form is 18 kJ mol$^{-1}$ lower in MNDO and is 0.8 kJ mol$^{-1}$ lower in ab initio [17]. A CI calculation [17], on the other hand conferred a stability on the 2H protomer greater than 99 kJ mol$^{-1}$, a result confirmed by other similar calculations [109,110]. It thus seems that the MNDO method leads to a slight overestimation of the stability of the 1H form. This remark had been advanced in the study of 1,2,3-triazole [111]. As in the case of this molecule, the calculated activation energy is high, at almost 290 kJ mol$^{-1}$. The structure of the transition state (fig. 5) shows a hydrogen migration out of the plane of the molecule, which is a general rule in 1–5 migrations [112–114].

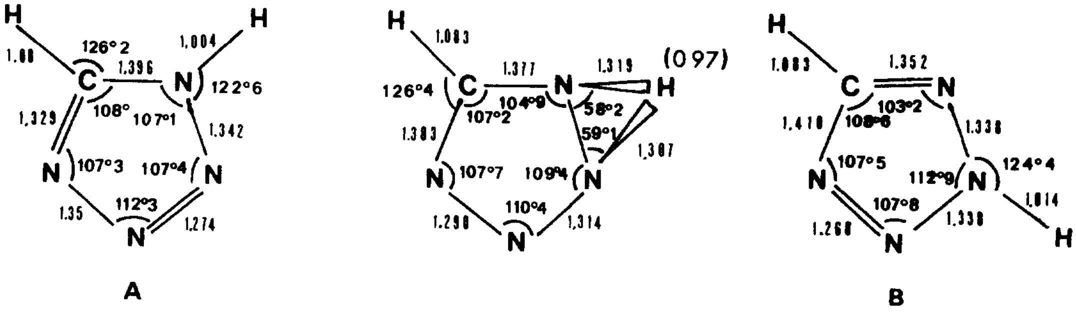

Fig. 5. MNDO structure of 1H- and 2H-tetrazole (A and B) and of the transition state between these two forms.

### 4.2. Thermal decomposition of tetrazole

If we consider only those transformations requiring minimum nuclear motion, i.e. opening, closure and 1–2 hydrogen migrations the thermal decomposition of tetrazole followed by the reorganization of $CN_2H_2$ can be schematically described as shown in fig. 6.

The energies of the minima and saddle points reported in this diagram are relative values in kJ $mol^{-1}$, compared to the most stable isomer, cyanamide ($+N_2$) calculated with ab initio (3-21G*) and MNDO (values in parentheses). As a result of the size of the molecule, the decomposition of the A and B forms of tetrazole were analyzed only with the MNDO method, reserving the ab initio method for the study of the potential energy hypersurface of the $CN_2H_2$ system.

This diagram shows the special importance of isodiazirine **1** which on the potential energy hypersurface is a common point for most $CN_2H_2$ reorganizations. This compound can be generated from both 1H (A) and 2H (B) tetrazoles either directly in a concerted reaction or in two steps with metastable intermediate minima corresponding to nitrene **2** and to nitrilimine **8**.

Fig. 7 shows the transition state structures (MNDO) of the four decomposition possibilities ($A \rightarrow \mathbf{1} + N_2$, $A \rightarrow \mathbf{2} + N_2$, $B \rightarrow \mathbf{1} + N_2$ and $B \rightarrow \mathbf{8} + N_2$). As predicted by the criterion of Hammond [115] for endothermic reactions, these structures are close to those of the decomposition products (**1**, **2** and **8**).

Based on the MNDO results on the degradation of 1H tetrazole, the pathway passing through nitrene imine **2** seems to be favored, since the two associated barriers (363 and 367 kJ $mol^{-1}$ in relation to tetrazole) are lower than that associated with the concerted process (407 kJ $mol^{-1}$).

As its 1H isomer, 2H-tetrazole (B) yields the linear structure **8** more easily than the ring **1**. The barrier between **8** and **1**, on the other hand, is slightly greater than that between B and **1**, so the concerted

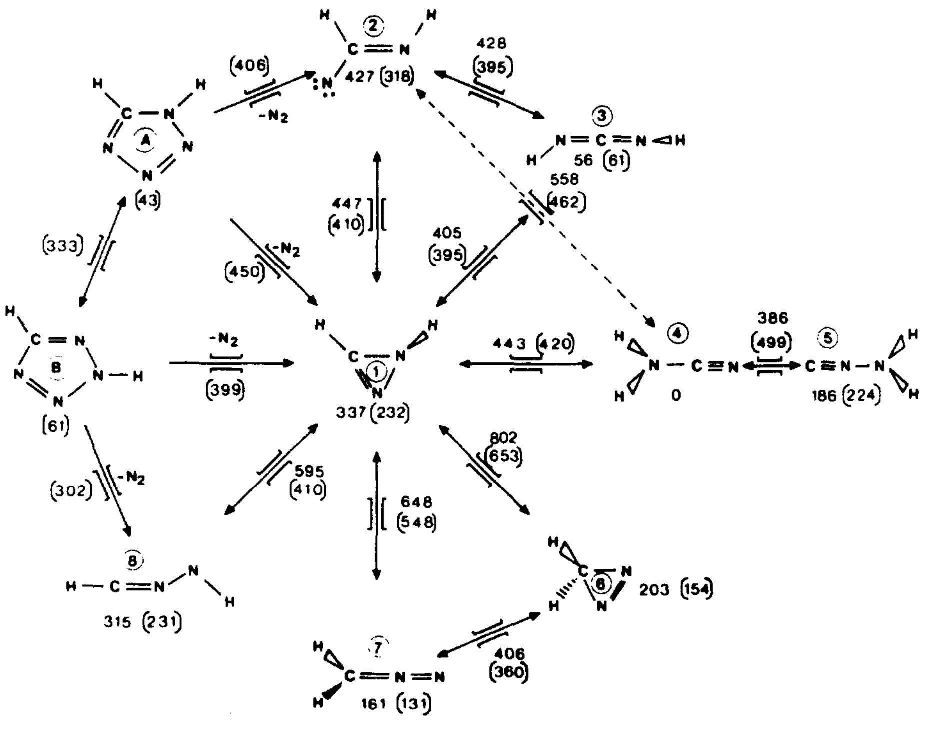

Fig. 6. Decomposition scheme of tetrazole. The energetic values (kJ $mol^{-1}$) of minima and saddle points are calculated with ab initio (3-21G*) method and with MNDO method (in parentheses).

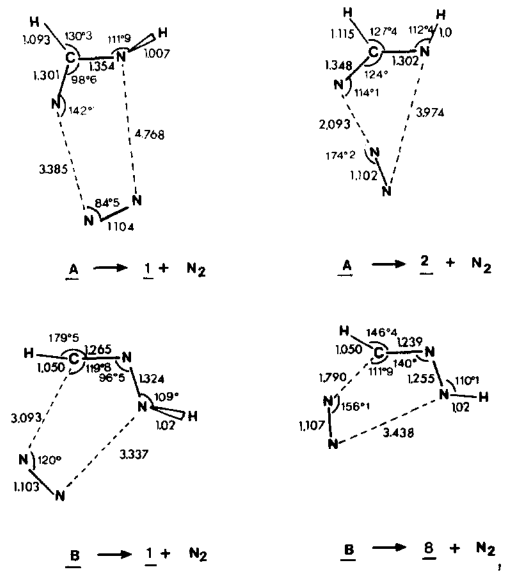

Fig. 7. MNDO transition state structures associated with the tetrazole (A and B) decomposition.

reaction $B \rightarrow \mathbf{1} + N_2$ is apparently preferential to $B \rightarrow \mathbf{8} + N_2 \rightarrow \mathbf{1} + N_2$. Similarly, the calculations suggest that this process is easier than involving A and nitrene **2**.

These conclusions must, however, be treated with caution, since the calculated energies are of the same order (except for B→**8**) and not all the differences are significant.

The transition state structures (fig. 7) show that the thermal decomposition of tetrazole begins by the rupture of the N(H)-N bond, followed by the progressive stretching of the other N-N bond. This is more pronounced in ring formation than in that of linear molecules **2** and **8**.

### *4.3. Rearrangements of the $CN_2H_2$ system*

As we mentioned before, the lowest saddle points on the $CN_2H_2$ potential energy hypersurface were determined. These values, as well as their relative energy values, are shown in fig. 6. The corresponding molecular structures (transition states) are shown in fig. 8.

It must be mentioned that our results obtained with single configuration wavefunction are only qualitative and must be considered as a first estimate of the energy barriers between the different minima of the $CN_2H_2$ hypersurface. To obtain a true picture of the potential surface and quantitative results, an MCSCF approach, as performed by Yoshimine et al. on the $C_3H_5$ system [116], is necessary. However to verify that the transition states can be described in a first approximation by a single determinant, we performed as for the minima, CI calculations (with CIPSI program) on the principal transition states. As it can be seen in table 5, the energies calculated at SCF level and the CI level are relatively close.

Carbodiimide **3** can be generated from nitrene **2** or from isodiazirine **1**. Even though the two activation energies are relatively close, the ab initio calculations indicate that the preferential pathway passes through nitrene **2** (A→**2**→**3**).

Cyanamide **4** can also be obtained from either **2** or **1**. In contrast to carbodiimide, the **1**→**4** pathway requires much less energy (115 kJ $mol^{-1}$ less) than **2**→**4**. Thus, the decomposition of 1H-tetrazole (A) into cyanamide **4** includes three steps: A→**2**→**1**→**4**.

The activation barrier separating **1** and **4** is comparable to those separating **1**, **2** and **3** (about 120 kJ $mol^{-1}$ in relation to **1**). As in the case of reactions **1**→**2** and **1**→**3**, it corresponds to a rupture of the N-N bond, the weakest in the ring. The activation barrier separating compounds **4** and **5** (386 kJ $mol^{-1}$, agrees with the value obtained by Vincent and Dykstra [30], the transition state structure also being very comparable.

On the other hand, the activation energies of transformations **1**↔**6**, **1**↔**7** and **1**↔**8** are much higher (465, 311 and 258 kJ $mol^{-1}$, respectively in relation to **1**). The first corresponds to the sigmatropic migration of a nitrogen hydrogen into carbon. The next two are the rupture of the C-N single bond, to which is added a hydrogen migration in the case of **1**↔**7**.

## 5. Conclusion

The comparison of experimental data obtained with the flash pyrolysis of tetrazole coupled with a photoelectron analysis and the theoretical study of the potential energy hypersurface of the $CN_2H_2$ system has enabled the following conclusions to be drawn:

- The thermal decomposition of tetrazole leads preferentially to cyanamide **4**, but also to the produc-

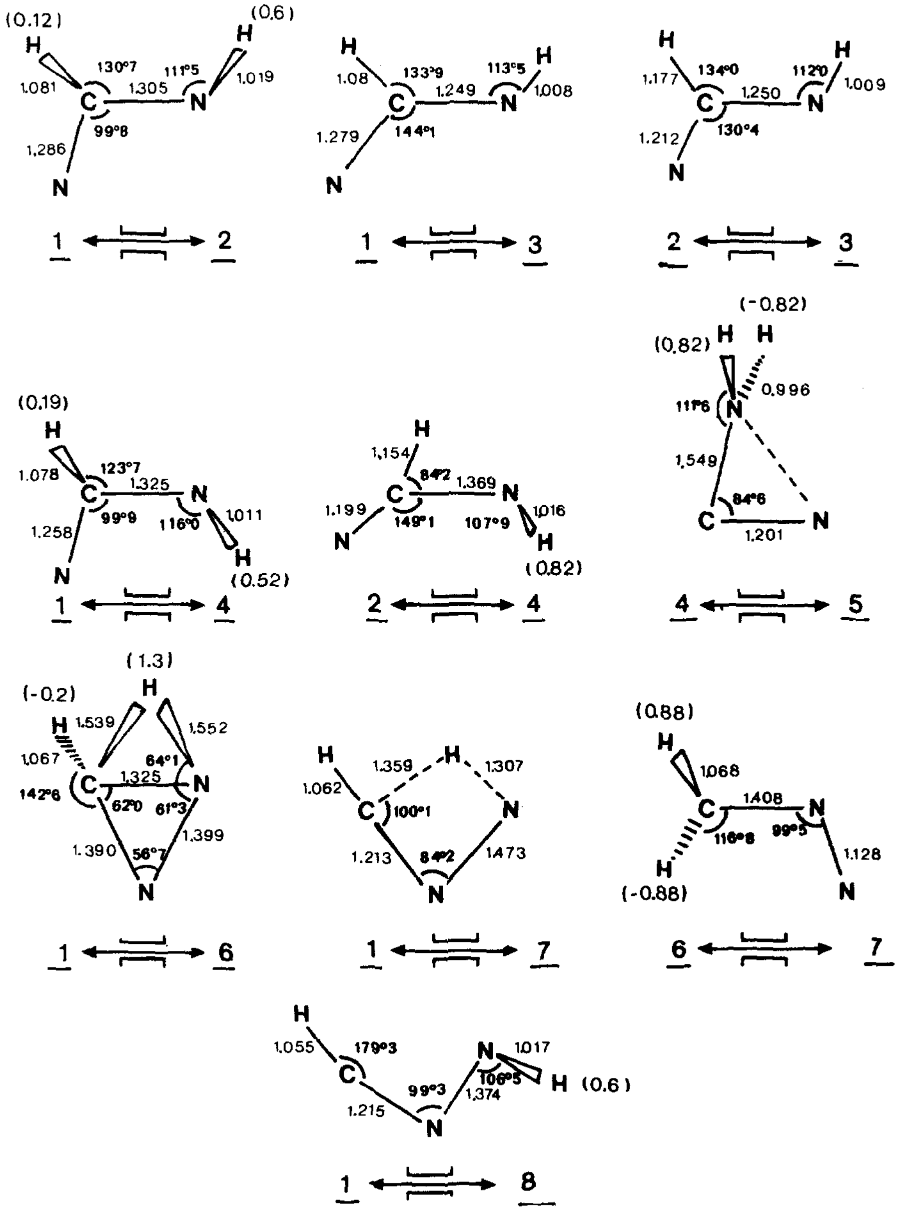

Fig. 8. Ab initio (3-21G*) transition state structures associated with the isomerization of the $CN_2H_2$ system. The values between parentheses are the ordinates of out-of-plane atoms.

tion of a small amount of diazomethane 7.

– Based on the theoretical results, the generation of these two molecules implies the transient formation of isodiazirine 1 (fig. 6).

– This metastable intermediate can be obtained either directly (concerted reaction) from 2H-tetrazole, or from 1H-tetrazole via a two-step reaction involving imino nitrene 2. It should be remembered that the two forms (1H) and (2H) can coexist in our experimental conditions, as a result of their comparable energies and a lower activation barrier than those involved in thermal degradation.

Table 5
Relative total energies (kJ mol$^{-1}$) of the transition states calculated at SCF level (3-21G basis set) and CI level (CIPSI method)

| Method | $1\leftrightarrow3$ | $1\leftrightarrow4$ | $1\leftrightarrow6$ | $1\leftrightarrow8$ |
|---|---|---|---|---|
| 3-21G* | 405 | 443 | 802 | 648 |
| CI | 442 | 506 | 732 | 632 |

- If we consider these different activation energies, which agree with the relatively high temperature of thermal decomposition (1000 K), isodiazirine can yield compounds **3**, **4**, **7** and **8** directly, as well as **5** and **6** indirectly. Carbodiimide **3**, the most thermodynamically stable after **4**, is too reactive even in our conditions of low pressure (1 Pa) to have a lifetime more than several tenths of a second required for its characterization. Isocyanamide **5** competes only with cyanamide and could thus not be observed because of its high energy (about 200 kJ mol$^{-1}$, see table 1). The same is true of diazirine **6** in comparison to diazomethane **7**. Finally, the low stability of nitrilimine **8** (about 300 kJ mol$^{-1}$ above **4**) did not enable it to be characterized by its photoelectron spectrum.

It must be remembered that these results are only qualitative due to the quality of our calculations (small basis set, energy minimisation at SCF level). Nonetheless the results probably reflect reality for the orders of activation energy barriers. It would seem that the correlation effects are relatively low, and that, in a first approximation, the structures of the minima and transition states can be described by a single determinant.

## 6. Experimental and computational details

The HeI photoelectron spectra were recorded on a PE spectrometer 0078 of Photoelectron Laboratories Ltd with argon and xenon used as internal calibrants (12.126 and 13.443 eV for $^2P_{1/2}$ and $^2P_{3/2}$ of Xe; 15.755 and 15.93 eV for $^2P_{1/2}$ and $^2P_{3/2}$ of Ar). Flash pyrolysis was carried out with a variable-temperature probe [117] allowing us to heat the vapor above 1300 K in a ceramic tube during a few tenths of seconds. The short pathway distance of about 5 cm between the end of the heating zone and the target chamber of the PE spectrometer allows the recording of photoelectron spectra of short-lived compounds ($\approx 0.1$ s) or rearrangement derivatives.

Firstly, the potential energy hypersurface of the tetrazole and the $CN_2H_2$ system were calculated with the MNDO method [118] which gives, for a reasonable price a quality of results close to ab initio double-zeta results [119,120]. A saddle point search algorithm [121–123] was used in these calculations, enabling us to find the lowest saddle point on the pathway between two minima on the potential energy hypersurface.

In a second study, we research the stationary points with the ab initio program MONSTERGAUSS [124,125]. The basis set was of the split valence 3-21G* type with d polarization orbitals on nitrogen. The molecular geometries were fully optimized with respect to all structural parameters (bondlengths and angles) by the Broyden–Fletcher–Goldfard–Shanno gradient method [126]. The minima and transition states were caracterized by the number of negative eigenvalues of the Hessian matrix (zero and one, respectively) [127], with the subroutine VA 05 included in the MONSTERGAUSS program.

The energies of compounds **1** to **8** and the ionization potentials were also calculated with configuration interaction by means of a program [128] using the CIPSI algorithm [129] (CI calculations for the ground states and the first ionic states) located after the HONDO program [130]. In these calculations, the geometries and basis set were the same as those of the MONSTERGAUSS calculations.

A variational zero-order wavefunction was built in an iterative selection of the most important singly and doubly excited determinants formed from the former reference subspace, the other ones being taken into account through a second-order Møller–Plesset perturbation. The configuration selection was based on the determinant coefficients in the correction of the zero-order function in the first order of the perturbation. In our case, the cutoff threshold was 0.02. So the reference subspace contained between 10 and 40 determinants. The number of determinants taken into account in the perturbative treatment was between $5\times10^5$ and $5\times10^6$.

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