223. Triaziridines

Part III[1])

Triaziridine, Azimine, and Triazene: A SCF Study of the Energy and Structure of N_3H_3-Isomers

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Summary

The portions of the N_3H_3 singlet potential energy surface corresponding to triaziridines (**1**), azimines (**2**) and triazenes (**3**) have been calculated by *ab initio* SCF using 3-21G, 6-31G, and 6-31G** basis sets. Minima and transition states were located by force gradient geometry optimization. The most important computation results are: 1) *Triaziridines* (**1**): The configuration at the 3 N-atoms is pyramidal. There are 2 stereoisomers, **1a** and **1b**. The *c,t*-isomer **1a** has less energy than the *c,c*-isomer **1b**. The 2 stereoisomerizations by N-inversion have rather high activation energies. The N,N bonds in **1** are longer and weaker (STO-3G estimation) than in hydrazine. The N-homocycle **1** exhibits less ring strain than the C-homocycle cyclopropane or three-membered heterocycles. 2) *Azimine* (**2**): All 6 atoms are in the same plane. There are 3 stereoisomers, **2a, 2b,** and **2c**. The order of ground state energies is $(Z,Z) < (E,Z) \ll (E,E)$. The 2 N,N bond lengths correspond to multiplicity $1^1/_2$. The electronic structure of **2** corresponds to a 1,3-dipole with almost equal delocalization of the 4 π-electrons over all 3 N-atoms. The negative net charge at the central N-atom is much less than that at the terminal N-atoms. Azimines should behave as π-donors in complexation with transition metals. 3) *Triazene* (**3**): All 6 atoms are in the same plane. There are 2 stereoisomers, **3a** and **3b**. The order of ground-state energies is $(E) < (Z)$. The stereoisomerization proceeds as pure N-inversion. N-Inversion has a high energy barrier. Inversion at N(1) is faster than at N(2). One of the N,N bond lengths is typical for a double, the other for a single bond. The electronic structure of triazene **3** entails rather localized π- and p-electron pairs at N(1),N(2) and at N(3). Triazenes should behave as p-donors in complexation with transition metals. 4) *N_3H_3-Isomers:* The order of ground-state energies is **3** < **2** < **1**. The energy differences between these constitutional isomers are much larger than between the stereoisomers of each. The [1,2]-H shifts for conversions of **2** to **3** and the [1,3]-H shift for tautomerization of **3** have relatively high activation energies; both shifts can be excluded as modes of thermal, unimolecular transformations.

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[1]) Part II, see [1].

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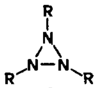
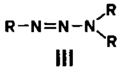
1. Introduction. – Homocycles containing only saturated N-atoms as ring members are an almost unexplored class of compounds, in contrast, for instance, to homocycles containing only saturated C-atoms. Theory predicts that lone-pair interactions destabilize such N-homocycles favoring their transformation to acyclic isomers or fragments with unsaturated N-atoms [2]. The only saturated N-homocycles available so far for experimental study are the triaziridines (**I**) with R = organic substituents [1] or with R = H as a Ag-zeolite complex [3].

The acyclic isomers of triaziridines (**I**), all of which contain unsaturated N-atoms, are better known, the 1,3-dipolar azimines (**II**) for more than a decade [4–6] and the triazenes (**III**) for a century [7], both with a variety of organic substituents R. At room temperature, some of the substituted triaziridines (**I**) slowly isomerize to the corresponding azimines (**II**) [1], and certain azimines (**II**) can be photolyzed to triazenes (**III**) [8]. So far, theoretical studies of N_3H_3 have been concerned only with a limited number of possible isomers. *Lathan et al.* [9] reported the STO-3G geometries of *c,t*- and *c,c*-triaziridine[3] (**1a** and **1b** resp.), the 4-31G//STO-3G energy difference between **1a** and **1b**, and the 6-31G*//STO-3G energy difference between **1a** and (*E*)-triazene (**3a**). The ($Z \rightarrow E$) isomerization of triazene (**3b**→**3a**) has been studied at the STO-3G level by *Howell & Kirschenbaum* [10]. *Hiberty & Leforestier* [11] have used minimal basis LCAO-MO functions, projected onto a complete basis of VB functions, to show that azimine (**2**) like other 1,3-dipoles has a strong diradical character[4].



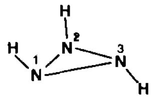
I

II

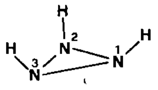


III

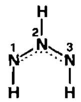
In this paper, we report our *ab initio* SCF calculations on seven of the possible isomers of N_3H_3, namely **1a**, **1b**, **2a**, **2b**, **2c**, **3a**, and **3b**.



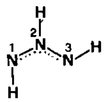
1a



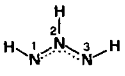
1b



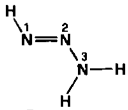
2a



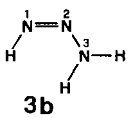
2b



2c



3a



3b

2. Calculations. – All calculations were performed with the aid of the MONSTERGAUSS 80 [13] program system, using the two split-valence gaussian basis set 3-21G [14] and 6-31G [15] as well as a split-valence plus polarization set 6-31G** [16]. For the geometry optimizations, the force method with analytical gradients [17] was used, along with the optimally conditioned minimization algorithm of *Davidon* [18]. All optimizations were terminated after the gradient length $G = \sqrt{\sum_{i=1}^{n} (\delta E/\delta q_i)^2/n}$ was reduced to less than $5 \cdot 10^{-4}$ mdyn.

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[3] *c,t*- = 1,2-*cis*-2,3-*trans*- (**1a**) and *c,c*- = 1,2-*cis*-2,3-*cis*-triaziridine (**1b**); **1a** could also be considered as *t,c*- or *t,t*-triaziridine. The choice of *c,t* is made on the basis of lexicographic preference (*c,t* < *t,c* < *t,t*).

[4] Prof. *P. v. R. Schleyer* informed us that he and his coworkers calculated several N_3H_3 and N_4H_4 isomers at the 3-21G//3-21G level [12].

For the geometry optimizations of the H-shift transition states, those points on the potential-energy hypersurface were located for which the matrix of the second derivatives of energy has a single negative eigenvalue. These points were identified by the finite difference procedure VAO5 of *Powell* [19]. For the geometry optimizations of the stereoisomerization transition states, one constraint was used in each case: With the triaziridines (**1**), the inverting N-atom and its 3 ligand atoms were kept in the same plane and with the triazenes (**3**), the inverting N-atom and its 2 ligand atoms were kept on a straight line.

3. Results and Discussion. – 3.1. *Structures and Relative Energies of N_3H_3-Isomers.* The N_3H_3 potential energy surface has many minima; apart from those belonging to **1**–**3**, there might be minima corresponding to structures such as H_3N^+-$N=N^-$, $H_2N-NH^+=N^-$, *etc.* In this work, we consider only species of which organic derivatives are known, namely those with the constitutions **1**–**3**. The geometries of all their possible stereoisomers **1a,b**, **2a–c**, and **3a,b**, calculated with the 3-21G and the 6-31G basis set, are shown in *Fig. 1*.

The total and the relative energies calculated at the 3-21G, 6-31G, and 6-31G**//3-21G (*i.e.* 6-31G** with 3-21G geometry) levels are listed in *Table 1*. In the 6-31G**

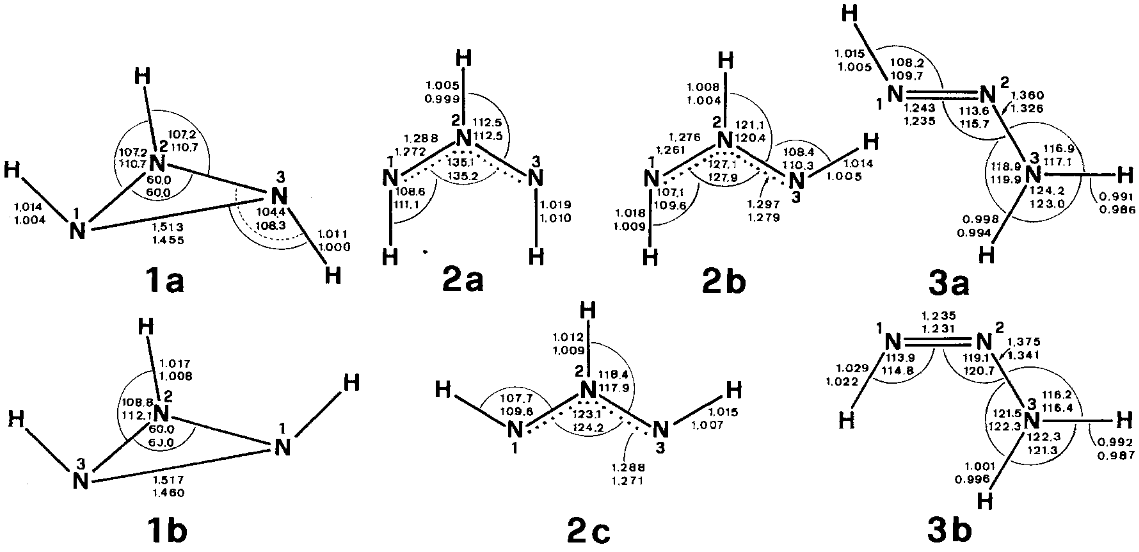


Fig. 1. *Optimized geometries of the 7 N_3H_3-isomers* **1**–**3**. The upper parameter values are obtained from the 3-21G basis set, the lower ones from 6-31G.

Table 1. *Total and Relative Energies of the 7 N_3H_3-Isomers* **1**–**3**

Molecule	Total energies [a.u.]			Relative energies [kJ/mol]		
	3-21G//3-21G	6-31G//6-31G	6-31G**//3-21G[a]	3-21G	6-31G	6-31G**
c,t-Triaziridine (**1a**)	– 163.98988	– 164.82314	– 164.93737	196	271	218
c,c-Triaziridine (**1b**)	– 163.96313	– 164.79618	– 164.91758	266	341	270
(*Z,Z*)-Azimine (**2a**)	– 164.00532	– 164.86766	– 164.97283	156	154	125
(*E,Z*)-Azimine (**2b**)	– 164.00169	– 164.86557	– 164.97013	165	160	132
(*E,E*)-Azimine (**2c**)	– 163.98346	– 164.84853	– 164.95648	213	204	168
(*E*)-Triazene (**3a**)	– 164.06462	– 164.92638	– 165.02054	0	0	0
(*Z*)-Triazene (**3b**)	– 164.05444	– 164.91200	– 165.00931	27	38	29

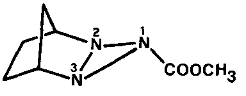
[a]) 6-31G**//3-21G: Calculated at 6-31G** level using 3-21G-optimized geometries as given in *Fig. 1*.

calculations, the 3-21G geometries were used in order to make the energies comparable to those of 6-31G** calculations of transition states in this work which were performed with 3-21G geometries. *Table 1* shows that all 3 calculation levels yield a similar order of relative energies for the 7 N_3H_3-isomers. The inclusion of polarization functions in the 6-31G calculation reduces the differences between cyclic and open-chain species. The same trend of energies has been calculated at similar approximation levels for most of the of C-, N- and O-containing three-membered rings and their open-chain isomers [9]. In the following discussion of the calculated energies of N_3H_3-isomers, we always use our 6-31G**//3-21G results unless mentioned otherwise.

3.1.1. *Triaziridines* (**1**). We calculate the N-atoms in both triaziridine stereoisomers **1a** and **1b** to have a pyramidal configuration with the N,H bond bent by 64–74° out of the ring plane (see *Fig. 1*). These values are similar to that found experimentally (microwave spectrum) for the N,H bond in aziridine (67.5° [20]).

In contrast to what was found in [9] at the STO-3G level, our calculations find the 2 non-equivalent N,N bonds (N(1),N(2) and N(1),N(3) = N(2),N(3)) in the *c,t*-isomer **1a** to have the same length (with both basis sets 3-21G and 6-31G, the difference lies outside the calculation precision). Furthermore, the N,N bond lengths in **1a** are almost equal to those in the *c,c*-isomer **1b**. Our 3-21G values (1.513 in **1a** and 1.517 Å in **1b**), are closer to the experimental ones (X-ray; 1.498 Å) in the triaziridine-Ag-zeolite complex [3] than our 6-31G results (1.455 in **1a** and 1.460 Å in **1b**).

The N,N bond lengths in triaziridines (**1a** and **1b**) calculated in this work with 3-21G and 6-31G (1.51–1.52 and 1.46 Å) and with STO-3G (1.48 Å [9]) are larger than or at least equal to that in hydrazine (1.46 Å [9]). In contrast, the STO-3G C,C bond lengths in cyclopropane (1.50 Å [9]) are smaller than that in ethane (1.54 Å [9]). This contrast is also born out by the available experimental values: The N,N bond lengths in the triaziridine-Ag-zeolite complex (X-ray) are 1.498 Å [3] and in the dialkyl-triaziridine-carboxylate **4** (X-ray) 1.46–1.49 Å [21]; in hydrazine (electron diffraction), however, this bond length is 1.453 Å [22]. The C,C bond lengths in cyclopropane (electron diffraction) are 1.510 Å [23]; in ethane (infrared spectral analysis), however, this bond length is 1.534 Å [24]. The fact that N-systems are characterized by longer bonds in 3-membered rings than in open chain compounds, in contrast to what is known for C-systems, could be due to the repulsive interactions of the lone pairs at the N-atoms.



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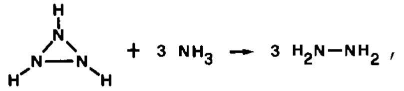
The *c,t*-isomer **1a** is calculated to have 52 kJ/mol less energy than the *c,c*-isomer **1b**. This might be attributed to the attractive 1,2-interaction between lone pairs and *cis*-located H-atoms [25] (twice in **1a**) and to the repulsive 1,2-interactions between *cis*-located H-atoms once in **1a**, three times in **1b** and those between *cis*-located lone pairs [26] (both three times in **1b** as compared to once **1a**). The repulsive factors should also operate in triaziridines with organic substituents. Experimentally (X-ray), a *c,t*-configuration has been found to be the thermodynamically more stable one in a crystal of **4**, where the 2 alkyl groups are fixed *cis* to each other by the C-bridges, while the acyl substituent at the third (easily invertible) N-atom is situated *trans* to the alkyl groups [1].

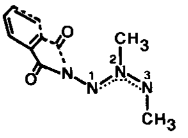
In order to obtain the bond-separation energy of *c,t*-triaziridine (**1a**) using the isodesmic reaction [9]



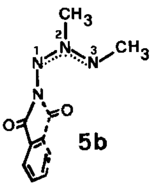
we calculated the total energies of NH_3 (−56.19499 a.u.) and of H_2NNH_2 (−111.18147 a.u.) by 6-31G**//3-21G. This together with the total energy of *c,t*-triaziridine (**1a**; −164.93737 a.u.) yielded a value of −58 kJ/mol for the bond-separation energy of **1a**. A 6-31G*//STO-3G calculation in the literature [9] reports a value of −35 kJ/mol for the same reaction. With compounds like **1a**, the bond-separation energies are a measure of the ring strain. The calculated 6-31G*//STO-3G values for cyclopropane and for aziridine are reported to be −110 and −93 kJ/mol, respectively [9]. Triaziridine (**1**), therefore, appears to be considerably less strained than the three-membered C-homocycle or corresponding heterocycles (see [9]).

3.1.2. *Azimines* (**2**). All 3 local minima of azimine (**2**) correspond to planar arrangements of all 6 atoms and to a bent chain of the 3 N-atoms (see *Fig. 1*). The largest N,N,N angle (135°) is found for the (*Z,Z*)-isomer **2a**, which could be due to a repulsive 1,3-interaction between H-atoms not present in **2b** and **2c**.

The calculated N,N bond lengths in **2** (1.26–1.29 Å) are close to the experimental (X-ray) distance between the CH_3-substituted N(2) and N(3) in (1*E*,2*Z*)- and (1*Z*,2*E*)-2,3-dimethyl-1-phthalimido-azimine (**5a** and **5b**; 1.263–1.268 Å [27]). The greater distance between N(1) and N(2) in the same compounds (1.30–1.33 Å [27]) is probably due to an inductive electron-withdrawing effect of the phthalimido group on N(1) (*cf.* [27]).



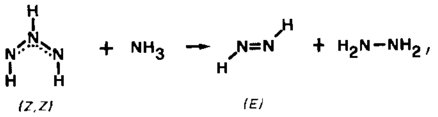
5a



5b

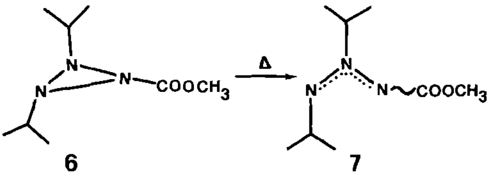
Surprisingly, the lowest-energy stereoisomer of unsubstituted azimine **2** is calculated to be the (*Z,Z*)-isomer **2a**, its energy being lower than that of the (*E,E*)-isomer **2c** by 43 kJ/mol and lower than that of the (*E,Z*)-isomer **2b** by (only) 7 kJ/mol. This order of ground-state energies may be attributed to the attractive 1,2- and 1,3-interactions between lone pairs and H-atoms [25] (twice 1,2- in **2a**, once 1,2- and once 1,3- in **2b**) as well as to the repulsive 1,2- and 1,3-interactions between lone pairs (once 1,3- in **2c**) and between H-atoms (once 1,2- in **2b**, twice 1,2- in **2c**, once 1,3- in **2a**). The presence of bulkier substituents, however, might easily tip the balance of stability in favor of the stereoisomer **2b** as has, in fact, been observed experimentally for **5a** and **5b**, both of which are (*E,Z*)-isomers [27].

To obtain the bond-separation energy of (*Z,Z*)-azimine (**2a**) using the isodesmic reaction [9]



we also calculated the total energy of (*E*)-diimide (−109.99987 a.u.). This, together with the values of NH_3, of H_2NNH_2 (see above), and of (*Z*,*Z*)-azimine (**2a**; −164.97283 a.u.) yielded a value of −35.5 kJ/mol for the bond-separation energy of **2a**. The fact that this value is relatively small implies that the strain in (*Z*,*Z*)-azimine (**2a**) is not significantly greater than the one in (*E*)-diimide plus the one in hydrazine. It further suggests that the sum of the azimine N,N bond multiplicities is about 3.

Azimines (**2**) have less energy than triaziridines (**1**); we calculate the lowest-energy azimine stereoisomer **2a** to have 93 kJ/mol less energy than the lower-energy triaziridine stereoisomer **1a**. This energy difference is of the same order of magnitude as the experimental (microcalorimetric) value for the ring opening of methyl *trans*-2,3-diisopropyl-triaziridine-1-carboxylate (**6**) to methyl (2*Z*)-2,3-diisopropyl-azimine-1-carboxylate (**7**), $\Delta H = 100 \pm 4$ kJ/mol [1].



6 **7**

3.1.3. *Triazenes* (**3**). Both local minima of triazene (**3**) correspond to planar arrangements of all 6 atoms and to a bent chain of the 3 N-atoms (see *Fig. 1*). Their bond lengths agree with former, less sophisticated calculations as mentioned in [10] and with experimental (X-ray) structure parameters of substituted triazenes [28].

We calculate (*E*)-triazene (**3a**) to have 218 kJ/mol less energy than the lower-energy triaziridine stereoisomer **1a** and only 29 kJ/mol less than (*Z*)-triazene (**3b**). Former calculations (6-31G*//STO-3G [9]) report values of 168 kJ/mol and 20 kJ/mol for these two energy differences. (*E*)-Triazene (**3a**) has 125 kJ/mol less energy than the lower-energy azimine stereoisomer **2a**. Thus triazenes (**3**) are of lowest ground-state energy among the N_3H_3-isomers considered here.

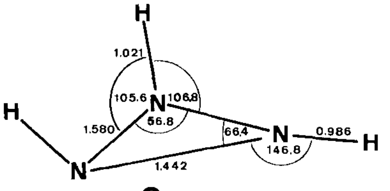
3.2. *Stereoisomerizations*. In this chapter we use our 3-21G values for the geometry of the transition states **8** and **9** and our 3-21G//3-21G as well as our 6-31G**//3-21G values for energy considerations (see *Table 2*).

Table 2. *Calculated Transition-State Energies of the Two N-Inversions in Triaziridines* (**2**) *and of Three N-Inversions in Triazenes* (**3**) *as well as the Corresponding Activation Energies*

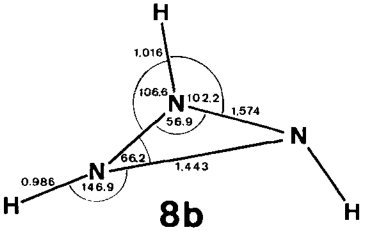
Conversion path	Transition state	Total energies [a.u.]		Activation energies [kJ/mol]	
		3-21G//3-21G	6-31G**//3-21G	3-21G//3-21G	6-31G**//3-21G
Inversion **1b**→**1a**	**8a**	−163.92437	−164.86996	102	125
Inversion **1a**⇆**1a**	**8b**	−163.93739	−164.87927	137	153
Inversion **3b**→**3a**	**9a**	−163.99092	−164.93346	166	199
Inversion **3b**→**3a**	**9b**	−163.96789	−164.91245	227	254
Inversion **3b**→**3a**	**9c**	−163.92468	−164.86456	340	380

3.2.1. *Triaziridine* (**1**). The *cis-trans* interconversion of triaziridine (**1**) has to occur by inversion at a pyramidal N-atom. With the assumption of planar configuration at this atom in the transition state, two such states have to be considered, namely **8a** and **8b**. State **8a** should be passed during the (*c,c*→*c,t*)-isomerization **1b**→**1a** and **8b** during the (*c,t*)-automerization **1a**⇆**1a**. In both states **8a** and **8b**, the N-ring forms an isosceles triangle with the N,N bond opposite to the inverting N-atom considerably stretched (1.58 Å) and the two other N,N bonds compressed (1.44 Å). Our calculated activation energies (see *Table 2*) for the conversions **1b**→**1a** and **1a**⇆**1a** are 102 and 137 kJ/mol, respectively (by 3-21G//3-21G), or 125 and 153 kJ/mol (by 6-31G**//3-21G). These values are of the same order of magnitude as the published theoretical inversion barriers for oxadiaziridine (161 kJ/mol [29]) and for oxaziridine (135 kJ/mol [30]); they are also in good agreement with the experimental value (racemization) for *N*-methyl-oxaziridine (135–142 kJ/mol [31]).

The experimental (^{1}H-NMR) inversion barrier at N(1) in the 2,3-dialkyl-triaziridine-1-carboxylate **6** is 62 kJ/mol [1], *i.e.* considerably lower than our calculated values for triaziridine itself. The transition state for the N-inversion is probably stabilized by a conjugating substituent like an acyl group relative to an H-atom.



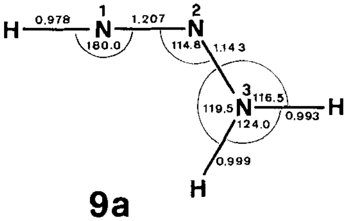
8a



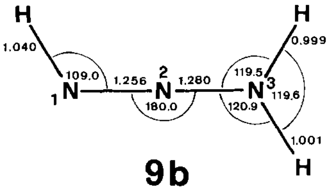
8b

3.2.2. *Triazenes* (**3**). *Howell & Kirschenbaum* [10] have shown by STO-3G calculations, that stereoisomerizations at N,N-double bonds substituted with a variety of groups including the NH_2-group as in triazene (**3**) proceed by inversion at an N-atom rather than by pure rotation around the N,N-double bond. At least 5 different transition states may be considered, all of which involve inversion, namely **9a** for inversion at N(1), **9b** for inversion at N(2), **9c** for inversion at N(2) plus rotation around N(1),N(2), **9d** for inversion at N(2) plus pyramidalization at N(3), and **9e** for inversion at N(2) plus rotation around N(1),N(2) plus pyramidalization at N(3). The authors [10] did not include inversion at N(1) *via* **9a** in their calculations, and of the other four pathways, they concluded inversion with pyramidalization *via* **9e** and **9d** to be preferred and of these two the more symmetrical transition state **9e** to be of lower energy.

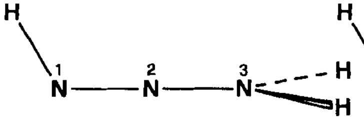
Our calculations on the stereoisomerization of triazenes (**3a**⇆**3b**) (see *Table 2*) reveal that **9a** and **9b** with all 6 atoms in a common plane are saddle points on the N_3H_3 energy surface, both of lower energy than **9c**–**9e**, and that **9a** (inversion at N(1)) is of lower energy than **9b** (inversion at N(2)). We find the activation energy for the stereoisomerization **3b**→**3a** to be high, namely *via* **9a** 166 (by 3-21G//3-21G) and 199 kJ/mol (by 6-31G**//3-21G), and *via* **9b** 227 and 254 kJ/mol. Thus, triazenes (**3**) are expected to be configurationally stable under thermal conditions. The difference between our results (no pyramidalization at N(3)) and those of *Howell & Kirschenbaum* [10] are due to the smaller basis set used in [10].



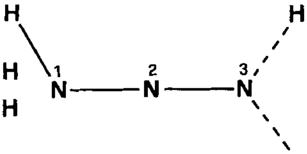
9a



9b



9c



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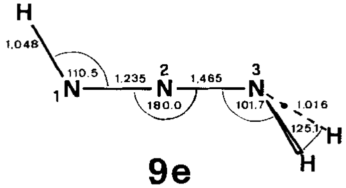


9e

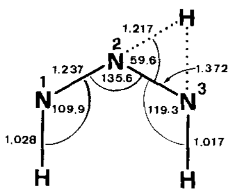
A transition state like **9e** which has the lowest energy within the **9c–e** set might, however, play a role as the preferred pathway of stereoisomerization when triazenes carry strongly electron-withdrawing substituents at N(1) as has been observed [32] in push-pull substituted azo compounds.

3.3. *Hydrogen Shifts.* [1,2]-H Shifts might be responsible for the isomerizations of azimines (**2**) to triazenes (**3**) and [1,3]-H shifts for the tautomerization of triazenes (**3**). The former reaction has been observed only photolytically [8], while the latter has often been studied thermally (see [33] and ref. therein). In this chapter we use our 3-21G values for the geometries of the transition states **10a, 10b,** and **11** and our 6-31G**//3-21G and 3-21G//3-21G values for energies (see *Table 3*).

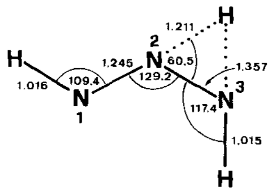
Table 3. *Calculated Transition-State Energies of the Two [1,2]-H Shifts in Azimines* (**2**) *and the [1,3]-H Shift in Triazene* (**3**) *as well as the Corresponding Activation Energies*

Conversion path	Transition state	Total energies [a.u.]		Activation energies [kJ/mol]	
		3-21G/3-21G	6-31G**/3-21G	3-21G//3-21G	6-31G**//3-21G
[1,2]-H shift **2a**→**3b**	**10a**	– 163.90451	– 164.86505	264	283
[1,2]-H shift **2b**→**3a**	**10b**	– 163.90768	– 164.87002	246	263
[1,3]-H shift **3a**⇆**3a**	**11**	– 163.98024	– 164.93041	221	236

3.3.1. *[1,2]-H Shifts in Azimines.* [1,2]-H Shifts transform (*Z,Z*)- and (*E,Z*)-azimine **2a** and **2b** into (*Z*)- and (*E*)-triazene **3b** and **3a**, respectively. Our geometry optimizations with 3-21G show the energetically most favorable transition state of the conversion of **2a** into **3b** and the one of **2b** into **3a** to be the coplanar arrangements **10a** and **10b**, respectively. The geometries of these states are similar to that which has



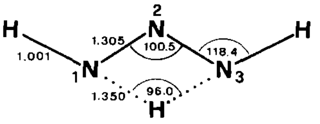
10a



10b

been calculated for the H-shift of (*E*)-diimide to aminonitrene [34]. According to our calculations using 6-31G**//3-21G, the activation energies for the two azimine-triazene rearrangements **2a**→**3b** and **2b**→**3a** are 283 and 263 kJ/mol, respectively, which makes both processes unlikely under thermal conditions. This correlates with the fact that only photolytic transformations of (substituted) azimines to triazenes have been observed so far [8].

3.3.2. *[1,3]-H Shifts in Triazenes.* Our geometry optimizations with 3-21G show the energetically most favorable transition state of the [1,3]-H shift in (*E*)-triazene (**3a**⇆**3a**) to be the coplanar symmetrical arrangement **11**. This process is very similar to the one which has been calculated for the [1,3]-H shift in formamidine [35] and in formic acid [36]. We did not consider a [1,3]-H shift in (*Z*)-triazene (**3b**), which must occur either with an inversion at N(1) or with a rotation around N(1),N(2), since such a process had previously been calculated to be of high energy in formamidine [37]. According to our calculations the energy barrier for the tautomerization of (*E*)-triazene (**3a**⇆**3a**) is 221 (by 3-21G//3-21G) or 236 kJ/mol (by 6-31G**//3-21G), values close to those which had previously been calculated for the analogous process in formamidine (248 kJ/mol (4-31G) [35]) and in formic acid (256 kJ/mol (4-31G) [36]). Even if electron-correlation effects (which tend to reduce the theoretical SCF energy barriers in [1,3]-H shifts by about 20% [36]) were included, the transition-state energy would remain too high to correlate with the experimentally observed rapidity of the tautomerizations in triazenes [33]. As a rationalization for this observed rapidity, a homolytic process has been considered on the basis of solvent effects [38]. A heterolytic process was calculated for the case of a [1,3]-H shift in formamidine: There, the transition-state energy was found to be reduced by solvent participation, either by solvation of the transition state [35] or by a catalytic effect [39]. Moreover, an intermolecular H-transfer *via* a dimeric transition state cannot be excluded (*cf.* [38]).



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3.4. *Electronic Properties of N_3H_3-Isomers.* Frontier molecular orbitals are frequently used in the evaluation of possible and in the interpretation of observed chemical reactions [40]. Knowledge about them is, therefore, of great interest for synthetic organic chemistry (see *e.g.* [41]). The 3 highest occupied orbital levels (HOMO) as well as the lowest virtual orbital level (LUMO) calculated with 6-31G** are presented as a correlation diagram for the seven isomers **1**–**3** in *Fig. 2.*

In triaziridines (**1**), all these orbitals are of σ-type; in **1b**, they are doubly degenerate as follows from the C_{3v} symmetry. In azimines (**2**) and triazenes (**3**), HOMO's and LUMO are π-orbitals. The σ-π separation in azimines (**2**) is much larger than in triazenes (**3**). This suggests different complexation properties with transition metals: Triazenes (**3**) should be lone-pair donors as in fact has been observed for many triazenido complexes [42]. Azimine (**2**), on the other hand, should be considered as π-donors, but azimine complexes are still unknown.

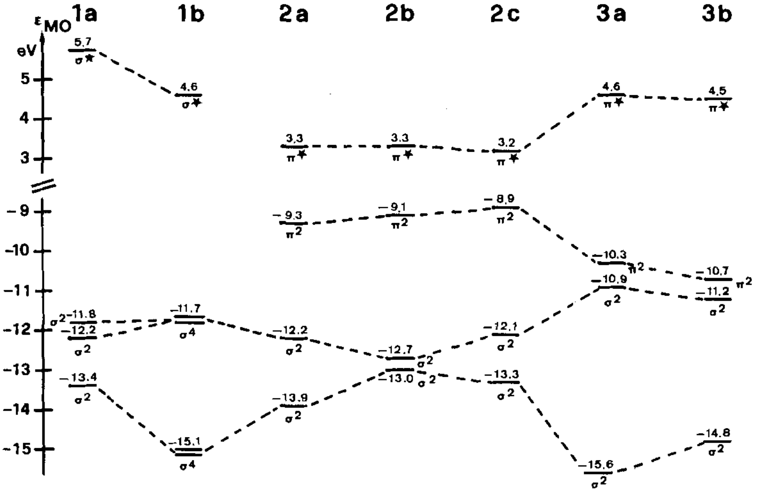

Fig. 2. *Orbital-correlation diagram for the 3 highest HOMO's and the lowest LUMO in the seven N_3H_3-isomers* **1–3** *at the 6-31G** level*

Net charges and π-populations, calculated with 3-21G, of the seven N_3H_3-isomers **1–3** are summarized in *Table 4*. We note a few interesting points: a) The negative net charge at the triaziridine N-atoms (–0.339 and –0.371 for **1a**, –0.313 for **1b**) is only about ⅓ of that at the ammonia N-atom (–0.876) or about ½ of that at the hydrazine N-atoms (–0.609). b) Net charges at the terminal N-atoms in azimines (**2**) are more negative than those at the central N-atom. This correlates with the observed lesser stability of 2-acylated [43] and 1,2-diacylated azimines [6] as compared to 1-acylated ones [5]. c) The π-populations reveal azimines (**2**) to be 4π-electron systems with almost equal delocalization over the 3 N-atoms. This justifies the formulation of azimines (**2**) with dotted second lines between the N-atoms, as used in the present and foregoing papers [4–6]. d) In triazenes (**3**), the central N-atom (N(2)) is almost uncharged and the π-

Table 4. *Net Charges (3-21G Values) at N- and H-Atoms of the 7 N_3H_3 Isomers* **1–3** *(π-Populations (3-21G Values) at N-Atoms in Parentheses) and Overlap Populations at N,N-Bonds (3-21G and STO-3G Values (the Latter for the Average of the Stereoisomers))*

Molecule	Net charges (π-populations)						Overlap populations	
	N(1)	N(2)	N(3)	H–N(1)	H–N(2)	H–N(3)	3-21G	STO-3G
1a	– 0.371		– 0.339	0.370		0.339	0.090[a])	0.188
1b	– 0.313			0.313			0.101	
2a	– 0.394 (1.380)	– 0.231 (1.239)		0.287	0.444		0.206	0.360
2b	– 0.416 (1.426)	– 0.230 (1.258)	– 0.373 (1.316)	0.288	0.412	0.319	0.168[a]) 0.224[b])	
2c	– 0.346 (1.359)	– 0.250 (1.282)		0.282	0.379		0.179	
3a	– 0.389 (1.193)	– 0.034 (0.957)	– 0.623 (1.850)	0.358	0.319	0.369	0.279[a]) 0.208[b])	0.425[a])
3b	– 0.336 (1.178)	0.012 (0.959)	– 0.658 (1.863)	0.336	0.267	0.379	0.343[a]) 0.180[b])	0.318[b])

[a]) N(1),N(2)-bond.
[b]) N(2),N(3)-bond.

populations show only a small contribution, −0.15, of the lone pair p-electrons of N(3) to the N(1),N(2)-π-system.

Table 4 also summarizes the overlap populations of the N,N-bonds in the 7 individual isomers **1**–**3** (calculated with 3-21G) as well as in the three N_3H_3 constitutions **1**, **2**, and **3**, each as average value of its stereoisomers (calculated with STO-3G). In azimines (**2**), these overlap populations, according to both levels of calculation, are in between those of the N,N-single bonds in triaziridine (**1**) and the N,N-double bond in triazene (**3**). To estimate the N,N-bond energies, we use the empirical relation between the overlap population P_{NN} as calculated at the STO-3G level (see *Table 4*) and the bond energy E_{NN} [44]: $E_{NN} = 3847.5 \cdot P_{NN}^3 - 985.6 \cdot P_{NN}^2 + 571.1 \cdot P_{NN}$[kJ/mol]. We obtain for triaziridine (**1**) $E_{NN} = 98.1$ kJ/mol, for azimine (**2**) $E_{NN} = 257.3$ kJ/mol, and for triazene (**3**) $E_{NN} = 360.0$ (N(1),N(2)) and 205.6 kJ/mol (N(2),N(3)). For hydrazine, E_{NN} has been calculated to be 159 kJ/mol [45]. Thus, the N,N-bonds in triaziridine are theoretically only 60% as strong as the N,N-bond in hydrazine.

4. Outlook. – For a full picture of the calculated properties of the N_3H_3-isomers, the ring opening of the triaziridine stereoisomers (**1a** and **1b**) to one or more of the azimine stereoisomers (**2a**–**c**) and the stereoisomerization among the azimines (**2a**$\leftrightarrows$**2b**$\leftrightarrows$**2c**) should be studied; for both processes diradicaloid transition states are expected [37]. Calculations of the exited states of the N_3H_3-isomers might also be useful in order to rationalize photochemical transformations. Because so far only substituted triaziridines, azimines and triazenes have been observed experimentally, it would be desirable to calculate the effect of organic substituents in these species.

The theoretical properties of the parent compounds, the N_3H_3-isomers, might stimulate further experimental work on their derivatives as follows: a) The expectation that triaziridine (**1**) and triazene (**3**) stereoisomers are configurationally stable encourages the search for stereoselective syntheses in this field. b) With respect to azimines (**2**), the calculated electronic properties suggest partners for 1,3-dipolar cycloaddition and for metal complexation. For such experiments, theoretical predictions of the electronic and steric substituent effects might be of interest.

Finally, looking at our results in the light of polyaza chemistry (chemistry of molecules containing N,N-bonds), analogous calculations of the N_4H_4 isomers are suggested[4]). They might stimulate the phantasy in developing synthetic methods for these mostly unknown compounds, namely for the stereoisomeric tetraazetidines, the 1- and 2-amino-azimines and the 1- and 2-tetrazenes, in form of organic derivatives.

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