171. Triazene: An *ab initio* Molecular-Orbital Study of Structure, Properties, and Hydrogen-Transfer Reaction Pathways

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Ab initio calculations of structure, properties, and tautomerization reactions of triazene (**1**) at the HF/3-21G// 3-21G, HF/6-31G*//6-31G*, HF/6-31G**//6-31G*, and MP2/6-31G**//6-31G* levels led to the following conclusions and predictions: *a)* Calculations of the ground-state structure of (*E*)- and (*Z*)-triazene (**1a** and **1b**, respectively) at various levels of theory show for both isomers C_1 geometry with a rather flat pyramidal configuration at N(3), and small energy differences (0.2–7.2 kJ/mol) between C_1 and C_s geometry, *i.e.* inversion at N(3) is a quasi-free process. With all levels of calculations, **1a** is found to be of lower energy than **1b** by 23–30 kJ/mol. *b)* Comparison of vibrational frequencies of (*E*)-diazene (**3**) calculated at the HF/3-21G level with experimental values reveals that HF/3-21G calculations are reliable for the prediction of vibrational frequencies of polyaza compounds, if corrected by a factor of 0.91. On this basis, the harmonic vibrational frequencies of **1a** and **1b** were predicted. *c)* For the rotation around the N(2)–N(3) bond of **1a** two conceivable transition states, **5a** (*syn*) and **5b** (*anti*) were located (HF/3-21G). The energy differences between **5a** or **5b**, and **1a** are in the order of magnitude of 50–56 kJ/mol and show a slight preference for the *anti*-mode, *i.e.* energy barriers for the N(2)–N(3) rotation are obtained comparable to those observed experimentally with substituted (*E*)-triazenes (**4**). *d)* Protonation of **1a** at N(1), N(2), or N(3) leads to **6a**, **6b**, and **6c**, respectively – the last one resembling an intermediate of formation of **1** from hydrogendiazonium ion (**7**) and ammonia (**8**). Energetically, the conjugate acids of **1a** follow the sequence **6a** < **6c** < **6b**. *e)* The preference of N(1) protonation of **1a** is also reflected in the relatively high gain of energy in the formation of H-bonded dimers of **1a** with H-bonds from N(3)–H to N(1). Calculations of three different H-bonded dimers **9a–c** of **1a** with the 3-21G basis show that an eight-membered cyclic dimer **9c** with two H-bonds from N(3)–H to N(1) is energetically most favoured (67.5 kJ/mol below two separate molecules of **1a**). This dimer might well be the starting situation of double intermolecular H-transfer leading to an automeric dimer **9c** *via* an energetically low-lying transition state **12**, thus offering a low-energy pathway for the known easy tautomerization of mono- or disubstituted (*E*)-triazenes. For **9c**⇌**9c**, the activation energy including correction for polarization and correlation effects as well as for vibration zero-point energy is estimated to be *ca.* 54 kJ/mol. *f)* A six-membered cyclic dimer **9b** of **1a** with two H-bonds from N(3)–H to N(2) might be involved for double H-transfer *via* a transition state **11** to a dimer **10** of (*E*, *Z*)-azimine (**2**). This process, however, turns out to be energetically highly disfavoured (estimated energy barrier for **9b**→**10**: 232 kJ/mol) in contrast to the reverse reaction (**10**→**9b** *via* **11**: 4 kJ/mol). This leads to the prediction that azimines bearing an H-atom at N(2) might be kinetically too instable for isolation, being, instead, easily tautomerized to triazenes by bimolecular H-transfer.

1. Introduction. – In [1], we reported the results of *ab initio* studies of energy, structure, and some isomerization reactions of N_3H_3 isomers at the HF/3-21G and HF/6-31G levels. Similar studies of N_1 to N_4 hydrides at the semiempirical MNDO and at the non-empirical 3-21G level have been performed also by others [2]. Among the studied molecules in both cases, the (*E*)- and (*Z*)-triazenes (**1a** and **1b**, respectively) demand further theoretical investigation, since several problems remained unsolved.

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1a   **1b**
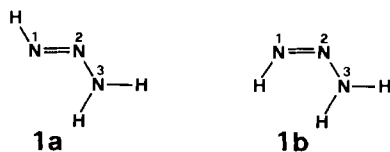
The first problem is concerned with the ground-state structure of **1a** and **1b**. Calculations at the 3-21G level resulted in C_1 geometry for both stereoisomers with an only slightly pyramidal configuration at N(3) and a very low barrier for inversion of this N-atom *via* a planar C_s geometry of the transition state (*cf.* [2]), whereas calculations with the larger split-valence 6-31G basis set converged in C_s geometry with planar N(3) configuration for the ground state of **1a** and **1b** (*cf.* [1]). Therefore, C_s geometry was used in [1] of **1** and its stereoisomerization. However, a clear decision of the N(3) configuration needs further calculations with inclusion of d-functions at N-atoms as used in the present study performed with the 6-31G* basis set.

Other open questions in connection with **1a** and **1b**, where theory might contribute, are prediction of their vibrational frequencies, calculation of the energy barrier of rotation around the N(2)–N(3) bond, and evaluation of the most likely protonation site of triazene (**1**). The last point is related to inspection of bimolecular H-transfer reactions of **1** which might be pathways for triazene-azimine isomerization (**1a**→**2**) *via* N(3)-to-N(2) H-transfer or for (*E*)-triazene tautomerization (**1a**⇌**1a**) *via* (N(3)-to-N(1)) H-transfer (see the *Scheme*) – the last mentioned process possibly being an attractive alternative to the energetically unfavourable intramolecular 1,3-H shift in **1a** as its tautomerization mode (*cf.* [1]).

Scheme
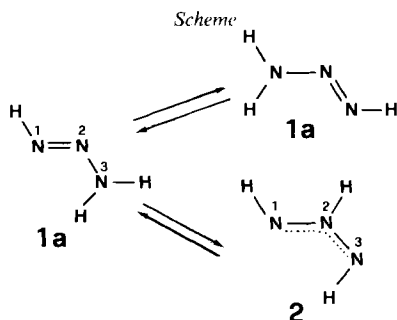
2. Calculations. – The molecular geometries of stationary points have been optimized by the force method with analytical gradient as implemented in the MONSTERGAUSS 80 program [3]. Since the polarization d-functions usually should be added to obtain the correct pyramidalization at N-atoms, we have employed both split-valence 3-21G [4] and split-valence plus d-functions 6-31G* [5] basis sets for determining the ground-state structure of **1a** and **1b**. To improve the thermodynamic data, we have recalculated single-point energies of different structures of **1** with the 6-31G** basis set on the basis of their optimized 6-31G* geometries. The electron-correlation effect has also been taken into account *via* second-order *Møller-Plesset* perturbation theory (MP2/6-31G**//6-31G*) using the GAUSSIAN 80 program [6]. For the remaining structures, the calculations are considered at either HF/6-31G**//3-21G or HF/3-21G//3-21G levels. For

simplicity, the last designator indicating the geometry employed will thereafter be omitted.

The transition-state structures of the bimolecular H-transfer reactions were located at such points of the energy hypersurface for which the matrix of the force constants has a single negative eigenvalue. The latter were calculated by the finite-gradient-difference procedure VAO5 [7]. Finally, the vibrational frequencies of **1a** and **1b** were determined at the harmonic level by the standard GF-matrix method [8].

3. Results and Discussion. – 3.1. *Structure and Energy of (E) and (Z)-Triazene* (**1a** und **1b**, respectively). The C_1 and C_s geometries of **1a** and **1b**, optimized at the 3-21G and the 6-31G* level, are summarized in *Table 1* and the corresponding energies calculated with HF/3-21G, HF/6-31G*, HF/6-31G**, and MP2/6-31G** in *Table 2*.

Table 1. *Optimized Geometric Parameters for* **1a** *and* **1b** *at the HF/3-21G and HF/6-31G* Levels*

| | (E)-Triazene (**1a**) | | | | (Z)-Triazene (**1b**) | | | |
| | HF/3-21G | | HF/6-31G* | | HF/3-21G | | HF/6-31G* | |
	C_1	C_s	C_1	C_s	C_1	C_s	C_1	C_s
Bond lengths [Å]								
N(1)–N(2)	1.241	1.243	1.217	1.222	1.234	1.235	1.213	1.218
N(2)–N(3)	1.368	1.360	1.348	1.318	1.385	1.375	1.350	1.326
H(1)–N(1)	1.015	1.015	1.008	1.006	1.029	1.029	1.022	1.021
H(2)–N(3)	0.999	0.998	1.002	0.997	1.002	1.001	1.004	0.999
H(3)–N(3)	0.992	0.991	0.996	0.989	0.994	0.992	0.996	0.990
Bond angles [°]								
H(1)–N(1)–N(2)	108.3	108.2	106.8	106.5	114.0	113.9	112.4	112.0
N(1)–N(2)–N(3)	113.4	113.6	115.7	113.9	118.9	119.1	117.8	119.8
H(2)–N(3)–N(2)	117.5	118.9	113.6	119.7	119.9	121.5	115.0	121.7
H(3)–N(3)–N(2)	115.5	116.9	111.0	116.9	114.7	116.2	110.6	116.8
H(2)–N(3)–H(3)	122.6	124.2	114.6	123.4	120.7	122.3	114.8	121.5
Torsion angles [°]								
H(1)–N(1)–N(2)–N(3)	179.0	180.0	177.1	180.0	0.9	0.0	0.4	0.0
H(2)–N(3)–N(2)–N(1)	9.9	0.0	21.3	0.0	14.1	0.0	21.5	0.0
H(3)–N(3)–N(2)–N(1)	166.8	180.0	152.2	180.0	170.0	180.0	153.6	180.0

Table 2. *Total* [a.u.] *and Relative Energies* [kJ/mol] *of Different Structures of* **1a** *and* **1b**, *Calculated with HF/3-21G// 3-21G, HF/6-31G*//6-31G*, HF/6-31G**//6-31G*, and MP2/6-31G**//6-31G**

	HF/3-21G// 3-21G	HF/6-31G*// 6-31G*	HF/6-31G**// 6-31G*	MP2/6-31G**// 6-31G*
(E)-triazene (**1a**)				
C_1 geometry	– 164.06471	– 165.01412	– 165.02508	– 165.52597
C_s geometry	– 164.06462	– 165.01139	– 165.02313	– 165.52427
$\Delta E(C_1 - C_s)$	– 0.2	– 7.2	– 5.2	– 4.5
(Z)-triazene (**1b**)				
C_1 geometry	– 164.05450	– 165.00266	– 165.01383	– 165.51726
C_s geometry	– 164.05444	– 165.00027	– 165.01214	– 165.51585
$\Delta E(C_1 - C_s)$	– 0.2	– 6.2	– 4.4	– 3.7
ΔE(**1b–1a**; C_1 geometry)	– 26.8	– 30.1	– 29.5	– 22.9

Comparison of the data within both *Tables 1* and *2* yields the following conclusions: *a)* With both basis sets 3-21G and 6-31G*, C_1 geometry with pyramidal configuration at N(3) is lower in energy than C_s geometry with planar N(3) for both stereoisomers. This clearly shows that the C_s geometry obtained at the 6-31G level for the ground state of **1a** and **1b** in [1] has to be considered as an artefact of this basis set and not as an indication of a constant trend towards planar configuration at N(3) in **1** when applying more elaborate calculation levels. This conclusion is in agreement with the one made for the configuration at the N-atom of vinylamine [9], where calculation at the HF/3-21G level had resulted in C_s geometry, but C_1 geometry was obtained at the HF/6-31G* level.

b) The energy difference between C_1 and C_s geometry for **1a** and **1b** is very small at the HF/3-21G level (0.2 kJ/mol in each case), but considerably larger in both cases when d-functions are included using 6-31G* geometries (see *Table 2*). However, this energy difference becomes smaller and smaller for both stereoisomers when including also the polarization p-function effect at H-atoms (HF/6-31G**) or even the electron correlation energy (MP2/6-31G**) in the calculations (see *Table 2*). This indicates that inversion at the pyramidal N(3) in triazenes (**1**) is expected to have generally a negligible energy barrier, since C_s geometry with planar N(3) is the transition state for N(3) inversion.

c) At all calculation levels, **1a** is lower in energy than **1b**, their energy difference being in the order of magnitude of 23–30 kJ/mol with the smallest value obtained by the most elaborate MP2/6-31G** calculations (22.9 kJ/mol).

d) In agreement with the low energy difference between C_1 and C_s geometry, the pyramidality at N(3) in the C_1 geometry is calculated to be only rather slight, least expressed at the HF/3-21G level (sum of bond angles around N(3) in **1a** 355.6°) and somewhat more at the HF/6-31G* (339.2°).

e) Interestingly, the H(1)–N(1) bond is slightly twisted out of coplanarity with the N(2)–N(3) bond at both levels of C_1 geometry optimization, namely in both stereoisomers in such a way that H(1) is looking in a direction opposite to H(2) and H(3) relative to the N(1)–N(2)–N(3) plane.

f) With all structures, as well as for C_1 as for C_s geometry, the N–N bond lengths (N(1)–N(2) and N(2)–N(3)) are calculated to be reduced by about 0.02–0.04 Å by incorporating d-functions *(Table 1)* in the basis set.

3.2. *Vibrational Frequencies of* **1a** *and* **1b** *Calculated at the HF/3-21G Level.* The computation of polyatomic vibration frequencies, using *ab initio* MO theory, has become a viable technique in recent years, especially at the HF/3-21G level [10]. Such studies, however, tend to result in somewhat large frequencies as compared to experimental values ([10] and literature quoted therein). Since vibrational frequencies of polyaza compounds have not been calculated in this way as yet, and because in the case of the molecules studied in the present work, **1a** and **1b**, no experimental values are available for comparison, we calculated first the harmonic frequencies of (*E*)-diazene (**3**) at the HF/3-21G level as a model case and compared them with those calculated at the HF/4-31G level [11] and with the experimentally observed ones [12] (see *Table 3*). It turns out that our calculated values are in the average by a factor of 1.10 larger than the experimental
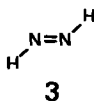
$$\text{H} \diagdown \text{N} = \text{N} \diagup \text{H}$$

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Table 3. *Calculated (HF/3-21G and HF/4-31G) and Experimental Harmonic Vibrational Frequencies* [cm⁻¹] *of (E)-Diazene* (**3**). Values in parentheses are the ratio $\nu_{cal.}/\nu_{pred.}$.

|		HF/3-21G[a])	HF/4-31G[b])	Exper.[c])	Assignment
Ag	ν_1	3427 (1.09)	3535 (1.13)	3128	N–H symmetric stretching
	ν_2	1748 (1.10)	1738 (1.10)	1583	Symmetric bending
	ν_3	1663 (1.09)	1681 (1.10)	1529	N–N stretching
Au	ν_4	1451 (1.13)	1844 (1.43)	1288	Torsion
Bu	ν_5	3474 (1.11)	3583 (1.14)	3137	N–H asymmetric stretching
	ν_6	1446 (1.09)	1444 (1.09)	1322	Asymmetric bending

[a]) This work.　[b]) From [11].　[c]) From [12].

Table 4. *Calculated (HF/3-21G) and Predicted[a]) Harmonic Vibrational Frequencies* [cm⁻¹] *of* **1a** *and* **1b**

	HF/3-21G		Predicted[a])		Assignment
	1a	**1b**	**1a**	**1b**	
ν_1	3924	3900	3567	3545 ⎫	N(3)–H stretching
ν_2	3730	3689	3391	3354 ⎬	
ν_3	3542	3337	3220	3034	N(1)–H stretching
ν_4	1768	1787	1607	1625	H–N(3)–H bending
ν_5	1646	1704	1496	1549	N(1)–N(2) stretching
ν_6	1610	1561	1464	1419	H–N(1)–N(2) bending
ν_7	1307	1289	1188	1172	N(1)–N(2)–N(3) bending
ν_8	1078	1073	980	975	N(2)–N(3) stretching
ν_9	1034	1027	940	934	H–N(1)–N(2)–N(3) out of plane
ν_{10}	649	644	590	585 ⎫	N(2)–N(3)–H bending
ν_{11}	603	504	548	458 ⎬	
ν_{12}	227	221	206	210	H–N(3)–H wagging

[a])　With the average scale factor $\nu_{(HF/3-21G)}/\nu_{pred.} = 1.10$, see the *Text*.

ones, but exhibit a smaller range of deviation from this average than the 4-31G values. This is in close agreement with conclusions in [10] obtained from the comparison of 3-21G results with experimental frequencies of small molecules containing H-, C-, N-, and O-atoms where the deviation of calculated from experimental values was found to be in the average *ca.* 10%. Thus, HF/3-21G calculations of vibrational frequencies of polyaza compounds turn out to yield reliable prediction results when corrected by a factor of 0.91 (inverse of 1.10 = $\nu_{(HF/3-21G)}/\nu_{pred.}$). Therefore, we undertook such calculations for **1a** and **1b**. The results are collected in *Table 4* together with the corrected (predicted) values and with the corresponding assignments from normal coordinate analysis.

3.3. *Rotation Barriers around the N(2)–N(3) Bond of* **1a**. Restricted rotation around the N(2)–N(3) bond is a frequently observed phenomenon with substituted (*E*)-triazenes (**4**, R = C-substituent, R' = H or C-substituent [13]). Experimental investigation of this phenomenon is easy since the speed of the N(2)–N(3) rotation corresponds to the NMR

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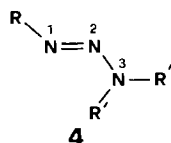
time scale at the normal temperature range (−50° to *ca.* 100°). Thus, rotational barriers can be derived from the coalescence temperature or from line-shape analysis of NMR spectra [14]. Depending on the electron-withdrawing effect of various substituents at N(1), energy barriers for the rotation around N(2)−N(3) have been found ranging from 45 kJ/mol in case of alkyl groups at N(1) up to 80 kJ/mol in case of acyl groups at N(1) ([15] and literature quoted therein).

With respect to the N(2)−N(3) rotation in unsubstituted **1a**, two modes of rotation might be differentiated, the '*syn*-mode' *via* the transition state **5a** and the '*anti*-mode' *via* **5b**. Both transition states, optimized at the HF/3-21G level, show in comparison to the 3-21G C_1 or C_s ground-state structures of **1a** shortening of N(1)−N(2), elongation of N(2)−N(3), and enhanced pyramidality at N(3) (sum of bond angles at N(3) 323.0° with **5a** and 318.3° with **5b**) as expected for a more pronounced p-electron localization at N(3).
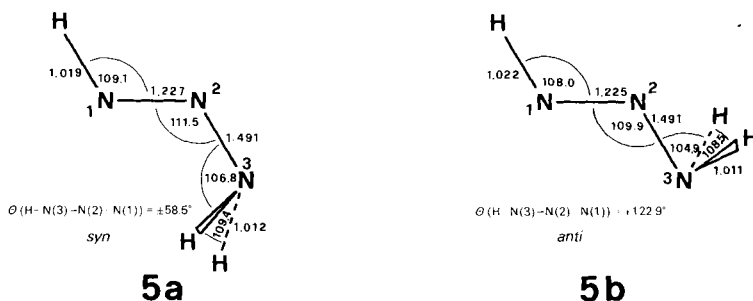

The energy barriers, calculated from the difference between the HF/3-21G or HF/6-31G** energies of **5a** and **5b**, respectively, and the corresponding energies of **1a** with optimized C_1 geometry [1] are of the same order of magnitude as the experimentally observed ones for substituted (*E*)-triazenes (**4**). They show a rather small preference for the '*anti*-mode' of rotation around N(2)−N(3) *via* **5b** (see *Table 5*).

Table 5. *Total Energies of the Transition States* **5a** *and* **5b** *of the N(2)−N(3) Rotation and Corresponding Energy Barriers in* **1a**

	Total energy [a.u.]		Energy barrier[a]) [kJ/mol]	
	HF/3-21G//3-21G	HF/6-31G**//3-21G	HF/3-21G	HF/6-31G**
5a	− 164.04321	− 164.99906	56.2	56.4
5b	− 164.04474	− 165.00147	52.2	50.1

[a]) Total energies of **1a** are −164.06462 a.u. (HF/3-21G//3-21G) and −165.02054 a.u. (HF/6-31G**//3-21G) [1].

3.4. Protonation Site of **1a**. Single protonation of **1a** might occur at N(1), N(2), or N(3) leading to the protonated species **6a**, **6b**, or **6c**, respectively, with structures optimized at the HF/3-21G level. The corresponding energies, calculated at HF/3-21G and HF/6-31G** are summarized in *Table 6* together with the respective proton affinities, calculated from the difference in energy between **1a** and **6a–c**.
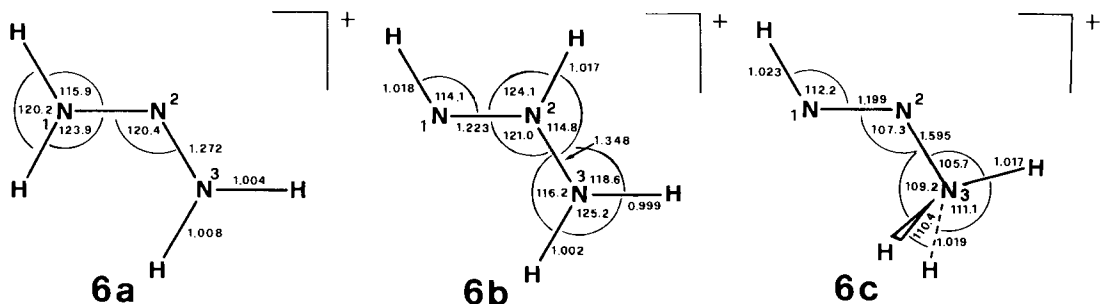
It turns out that N(1) is the energetically most favoured protonation site of **1a** and N(2) the least favoured one. Protonation at N(3) is only by 63.2 kJ/mol (3-21G) or 79.8 kJ/mol (6-31G**), respectively, less favoured than that at N(1) and leads to a species **6c** with an unusually long N(2)–N(3) bond of 1.595 Å, thus resembling a strong complex between hydrogendiazonium ion (**7**) and ammonia (**8**). The system **7** plus **8** (total energy – 164.37339 a.u. at the HF/3-21G level) is only by 81.6 kJ/mol higher in energy than **6c**, which actually corresponds to the intermediate of formation of (substituted) triazenes by addition of (arene) diazonium ions to amines [16] and its reverse reaction, fragmentation of (substituted) triazenes into (arene) diazonium ions, and amines under strongly protic conditions [17].

Table 6. *Total Energies of the Three Isomers* **6a–c** *of Protonated* **1a** *and Relevant Proton Affinities*

Species	Total energy [a.u.]		Proton affinity[a]) [kJ/mol]	
	HF/3-21G//3-21G	HF/6-31G**//3-21G	HF/3-21G	HF/6-31G**
N(1)-Protonated **6a**	– 164.42856	– 165.37836	955.5	939.4
N(2)-Protonated **6b**	– 164.38000	– 165.33377	828.0	822.4
N(3)-Protonated **6c**	– 164.40449	– 165.34795	892.3	859.6

[a])　See *Footnote* of *Table 5* for energies of **1a**.

3.5. *Bimolecular H-Transfer in H-Bonded Dimers of* **1a**. Intramolecular 1,3-H shift as a mode of tautomerization **1a**⇌**1a** and intramolecular 1,2-H shifts as a mode of isomerization **2**→**1a** (*cf.* the *Scheme*) have been both shown by *ab initio* SCF calculations [1] to be rather high-energy processes which make them unlikely under thermal conditions. In contrast, intermolecular H-transfer reactions *via* dimeric H-bonded intermediates and dimeric transition states could be alternative pathways for such isomerizations.

We, therefore, optimized the geometry of three possible H-bonded dimers of **1a** as starting situations for H-transfer reactions, namely the open dimer **9a**[1]) with one H-bond between N(3)–H of the first and N(1) of a second molecule **1a**, and two cyclic dimers each with two intermolecular H-bonds, namely the dimer **9b** with H-bonds from N(3)–H to

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[1])　The open dimer **9a** is just one arbitrarly chosen representative of the entire class of possible open dimers of **1a**.

9a

9b

9c

10
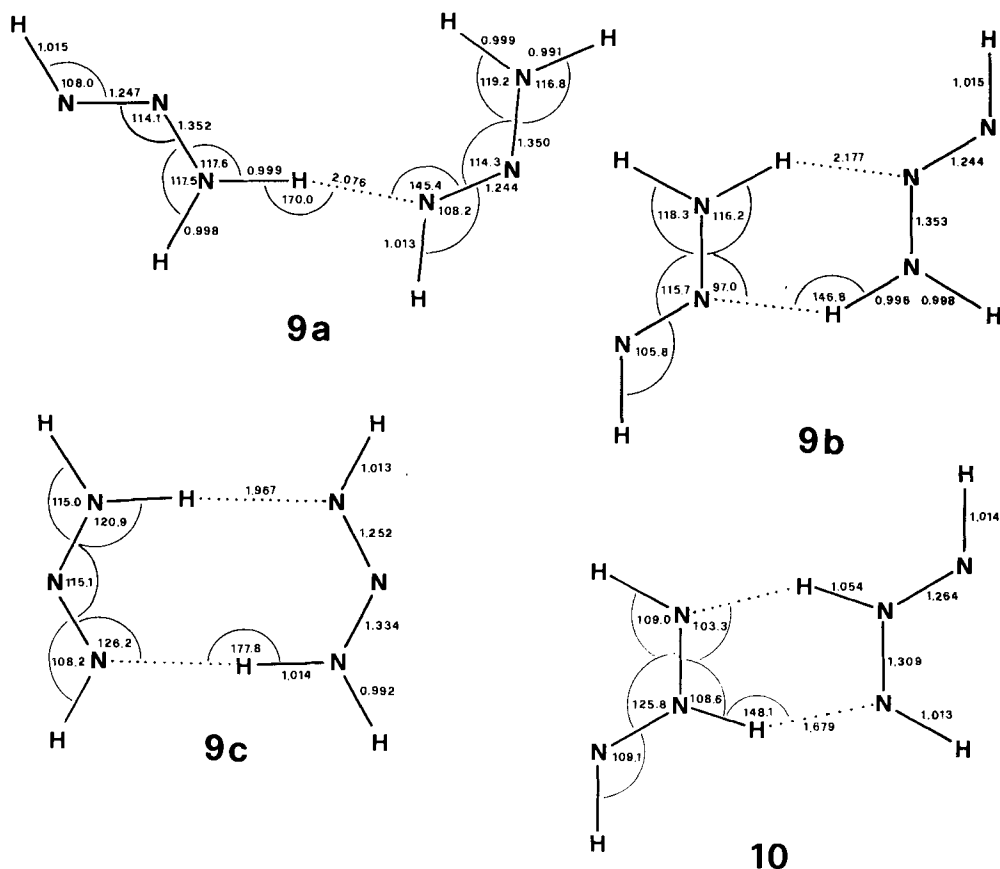
N(2) forming a six-membered ring system, and the dimer **9c** with H-bonds from N(3)—H to N(1) forming an eight-membered ring system. In addition, a cyclic dimer **10** of (E, Z)-azimine (**2**) was calculated with H-bonds from N(2)—H to N(3) as it would be expected as the product of double H-transfer reactions of **9b**.

The total energies of these dimers, calculated at the HF/3-21G level, and their relative energies as compared to that of two separated molecules of **1a** as standard are summarized in *Table 7*. One sees that the open dimer **9a**[1]) and the six-membered cyclic dimer **9b** are of comparable energy and contribute only a gain of energy of 30–40 kJ/mol in comparison to the standard of two separated molecules of **1a**, whereas the eight-membered cyclic dimer **9c** is favoured by 67.5 kJ/mol in comparison to the standard. The (E, Z)-azimine dimer **10** lies high up in energy.

The scale of energy of the dimers **9a–c** is in agreement with our findings concerning the protonation site of **1a** (see *Chapt. 3.4*) in as much as N(3)-to-N(1) H-bonding (as in **9a** and **9c**) is clearly favoured against N(3)-to-N(2) H-bonding (as in **9b**).

The cyclic dimers **9b** and **9c** are possible intermediates in bimolecular H-transfer reactions of **1a**. Similar dimers as **9c** have been taken also in consideration for tautomerization of formic acid [18] and 2-pyridone [19]. The six-membered cyclic dimer **9b** would be involved in the isomerization **1a**→**2** via the transition state **11** which leads to the (E,

Table 7. *Energy Characteristics Relevant to Dimer Formation and Bimolecular H-Transfer Reactions of* **1a** *and of* **2** *at the HF/3-21G//3-21G Level*

|		Total energy [a.u.]	Relative energy[a]) [kJ/mol]
(*E*)-Triazene dimers	**9a**	− 328.14147	− 32.1
	9b	− 328.14413	− 39.1
	9c	− 328.15495	− 67.5
(*E,Z*)-Azimine dimer	**10**	− 329.04957[b])	209.2
Double H-transfer			
Transition states	**11**	− 328.04802	213.2
	12	− 328.12685	6.3
Activation energy			
9b → **11** → **10**			252.3 (232[c]))
9c → **12** → **9c**			73.8 (54[c]))
10 → **11** → **9b**			4.0

[a]) Relative energies with respect to two separate molecules of **1a**: − 328.12924 a.u. at HF/3-21G//3-21G [1].
[b]) Total energy of **2** is − 164.001069 a.u. at HF/3-21G//3-21G [1]; thus, the dimer **10** lies by − 124.5 kJ/mol below two separate molecules of **2**.
[c]) Predicted activation energies including correction for polarization and correlation effects as well as for vibration zero-point energy (see the *text*).

Z)-azimine dimer **10**. The eight-membered cyclic dimer **9c** would be involved in the tautomerization **1a** ⇌ **1a** *via* the transition state **12** which leads to an automeric dimer **9c**.

Both transition states **11** and **12** have been optimized at the HF/3-21G level. Their energies (see *Table 7*) show that **11** is much less favoured than **12**, the first being higher in energy by 213.2 kJ/mol than two separated molecules of **1a** and the second one only
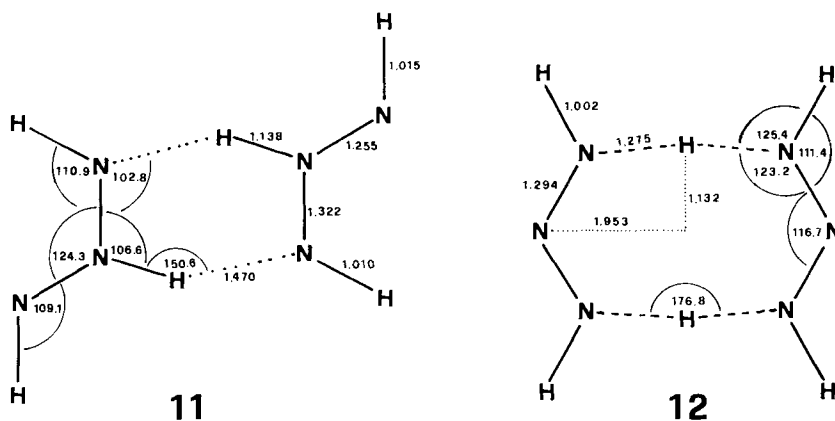
higher by 6.3 kJ/mol. This means that in relation to the starting situation of H-bonded dimers the double H-transfer reaction from **9b** *via* **11** to **10** needs a (calculated) activation energy of as high as 252.3 kJ/mol, making such a process rather unlikely under thermal conditions (for the reverse reaction, see below). In contrast, the double H-transfer reaction starting from **9c** *via* **12** to **9c** has a calculated activation energy of only 73.8 kJ/mol. Actually, both activation-energy values should be corrected by polarization and

correlation effects as well as by the vibration zero-point energy. The first two effects act for the considered type of reactions normally into opposite directions [20]. In our case, they even might cancel each other as has been found for the closely related H-transfer reaction in dimeric formic acid [18]. The zero-point energy contribution is assumed to be in the same order of magnitude as has been calculated for the formic acid dimer case [18], namely of *ca.* −20 kJ/mol. With this value, the predicted activation energies of double H-transfer reactions from cyclic (*E*)-triazene dimers to an (*E, Z*)-azimine dimer or an automeric (*E*)-triazene dimer (**9b** *via* **11** to **10**, or **9c** *via* **12** to **9c**, respectively) are predicted to be *ca.* 232 kJ/mol and 54 kJ/mol, respectively (see *Table 7*). The latter value is in the same order of magnitude as the experimentally (¹H-NMR) determined activation energy of tautomerization of (*E*)-1,3-dimethyltriazene (**13**; 39 kJ/mol) [21]. For this reaction, a second-order rate constant was obtained from ¹H-NMR line-shape analysis [21], as it has also been postulated [22] in other cases of intermolecular H-transfer as mode of (*E*)-triazene tautomerization. However, with certain aryl-substituted (*E*)-triazenes, first-order rate constants for tautomerization have been found experimentally [21].
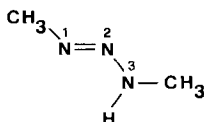
13

The (*E,Z*)-azimine dimer **10** is remarkably lower in energy than two separate molecules of **2**, namely by 124.5 kJ/mol. Correspondingly, the activation energy for its double H-transfer reaction *via* **11** to the dimer **9b** is calculated to be only 4 kJ/mol. This means that theory predicts that azimines with an H-atom at N(2) are expected to be kinetically too instable to be isolated.

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