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148. Triaziridines

Part V[1])

A Semiempirical MNDO Study of Nitrogen Inversion and Amide Rotation in Formyltriaziridines

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Since we found certain structural features of triaziridine (**1**) obtained by MNDO calculations to be in qualitative agreement with those derived earlier from *ab initio* calculations, we used the MNDO method to derive properties of formyltriaziridine (**2**) and 1-formyl-2,3-diisopropyltriaziridine (**3**) as models for the preparatively known 2,3-dialkyl-triaziridine-1-carboxylates **4** and **5**. The main results are: *a)* The triaziridine N-atoms with H, alkyl, or formyl as substituents (see **2** and **3**) are pyramidal. N(1) carrying the formyl group is flatter than N(2) and N(3) with H or alkyl substitent. Bond lengths and angles at N(2) and N(3) are almost identical with those calculated for the N-atoms of **1**. *b)* The MNDO inversion barriers at the H-substituted N(2) and N(3) of **2** are higher than those at the formyl-substituted N(1), but similar to the *ab initio* barriers at the N-atoms of **1**. *c)* The MNDO inversion barriers at N(1) of **2** and **3** are 53 to 92 kJ/mol, whereas the rotation barriers around the N(1)–C(4) bond are 7 to 23 kJ/mol; thus, the previously observed dynamic NMR phenomena in *trans*-2,3-diisopropyltriaziridine-carboxylates (**5**) can now be assigned to the slowing down of N(1) inversion rather than N(1)–C(4) rotation.

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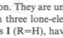
1. Introduction. – Triaziridines (**I**) are a sufficiently novel class of compounds to warrant some caution in applying chemical intuition. They are unusual inasmuch as they are three-membered non-carbon homocycles with three lone-electron pairs on the ring atoms. The two stereoisomeric parent triaziridines **I** (R=H), have been studied recently by *ab initio* SCF MO calculations [2]. However, aside from an Ag-zeolite complex of N_3H_3 [3], the only samples of triaziridines (**I**) known so far are those which carry C substituents, namely an alkoxycarbonyl and two alkyl groups (see **IIa**) [4] [5][3]). We therefore under-

I



IIa R = alkyl, R′ = *O*-alkyl
b R = H or i-Pr, R′ = H

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

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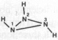
[3]) While the present manuscript was in preparation several further triaziridines have been prepared, and the ^{15}N-NMR spectra of some triaziridines have been studied [6].

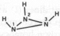
took a theoretical study on triaziridine derivatives which are simple and yet have sufficient similarity to these known compounds. We report here the results of semiempirical MNDO calculations on the two formyltriaziridines **IIb** with respect to *a)* the configuration (pyramidal or planar) at the H-, alkyl-, and acyl-substituted N-atoms, *b)* the relative energies of stereoisomers, *c)* the barriers to inversion at the two types of N-atoms (acylated and non-acylated ones), and *d)* the barriers to internal rotation of the acyl substituent around the N–C(=O) bond.

2. Objects and Methods. – Among the different less demanding levels of MO calculations, we chose the MNDO approximation, because it had been applied successfully to aziridine [7] and diazirines [8]. To test the validity of this method for our N_3-homocyclic system, we first applied it to the ground-state geometries and energies of *c,t*- (**1a**) and *c,c*-triaziridine (**1b**)[4], which had recently been calculated [2] by *ab initio* SCF MO. A comparison of the MNDO results with those of the *ab initito* calculations showed a qualitative agreement (see *Chapt. 3*).

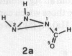
Based on this, it was decided to calculate the following somewhat larger molecules by MNDO: *t,c*-formyltriaziridine (**2a**), *c,t*-1-formyltriaziridine (**2b**), *c,c*-1-formyltriaziridine (**2c**), *t,c*-1-formyl-2,3-diisopropyltriaziridine (**3a**), *c,t*-1-formyl-2,3-diisopropyltriaziridine (**3b**), and *c,c*-1-formyl-2,3-diisopropyltriaziridine (**3c**)[4]) (see *Chapt. 4*). For **1a** to **2c**, the molecular ground-state geometries were optimized without constraints by the gradient method of *Davidon et al.* [9], as implemented in the QCPE version of the MNDO program [10]. The same procedure was applied to **3a** to **3c**, except that standard C–C and C–H bond lengths, tetrahedral angles, and staggered dihedral angles were used as constraints within the i-Pr groups.



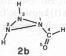
1a



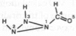
1b



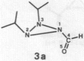
2a



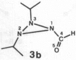
2b



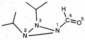
2c



3a



3b



3c

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[4] *c,c*-, *c,t*-, *t,c*-, and *t,t*-triaziridines = 1,2-*cis*-2,3-*cis*-, 1,2-*cis*-2,3-*trans*-, 1,2-*trans*-2,3-*cis*-, and 1,2-*trans*-2,3-*trans*-triaziridines, respectively. The atom numbering is determined by the constitution (*cf.* IUPAC rules). When there is a choice of numbering then the one which leads to the lexicographically preferred descriptor (*c,c* < *c,t* < *t,c* < *t,t*) is used (see [2], Footnote 3).

Using the same method and, for **3a** and **3b**, applying the same i-Pr constraints, the barriers of pyramidal N-inversions were calculated for certain values of the torsion angles R–N–N–N (R=CHO or H), this value being increased in steps of 10°, and the barriers of N(1)–C(4) rotation for certain values of the torsion angle O(5)–C(4)–N(1)–N(2), this value being increased in steps of 15°. In both barrier calculations, the rest of the geometry was reoptimized without constraints.

3. MNDO Results on the Triaziridines 1a and 1b and Comparison with *ab initio* Results.

– *Table 1* shows the results of our MNDO calculations on the ground-state structure of the two stereoisomers of **1** together with our previous results [2] of *ab initio* SCF calculations using the 6-31G basis set (the best data available). As can be seen, the two methods lead to rather similar results, insofar as the N–N bond lengths differ by not more than 4%, the degree of N-pyramidality by not more than 3%, and the differences in energies[5] by not more than 17% (6-31G//6-31G).

Table 1. *N–N Bond Lengths and Bond Angles around N-Atoms in* t,c- *and* c,c-*Triaziridines* **1a** *and* **1b**, *respectively.* Comparison of values calculated at the MNDO level with those at the *ab initio* level (6-31G).

Bonds and bond angles	**1a**		**1b**	
	MNDO	6-31G [2]	MNDO	6-31G [2]
Bond	*Length* [Å]			
N(1)–N(3)	1.401	1.455	1.408	1.460
N(2)–N(3)	1.401	1.455	1.408	1.460
N(1)–N(2)	1.409	1.455	1.408	1.460
H–N(1)	1.030	1.004	1.033	1.008
H–N(2)	1.030	1.004	1.033	1.008
H–N(3)	1.027	1.006	1.033	1.008
Bond angle	*Angle size* [°]			
N(2)–N(1)–N(3)	60.1	60.0	60.0	60.0
H–N(1)–N(2)	116.3	110.7	114.9	108.8
H–N(1)–N(3)	110.9	110.7	114.9	108.8
N(1)–N(2)–N(3)	60.1	60.0	60.0	60.0
H–N(2)–N(1)	116.3	110.7	114.9	108.8
H–N(2)–N(3)	110.9	110.7	114.9	108.8
N(1)–N(3)–N(2)	59.8	60.0	60.0	60.0
H–N(3)–N(1)	112.0	108.3	114.9	108.8
H–N(3)–N(2)	112.0	108.3	114.9	108.8
Pyramidality	*Sum of angle sizes* [°]			
at N(1)	287.3	281.4	289.8	284.2
at N(2)	287.3	281.4	289.8	284.2
at N(3)	283.8	276.6	289.8	284.2
Energy	*Value* [kJ/mol]			
ΔH_f	312.5	397.0[a]	365.8	467.0[a]
$\Delta\Delta H_f$ (**1b–1a**)[5]	53			
$\Delta E_{tot.}$ (**1b–1a**)[5]		70		

[a] 3-21G Values [11].

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[5] We do not compare MNDO enthalpies (ΔH_f) with *ab initio* total energies ($E_{tot.}$), their standards being different (*cf.* [11]), but rather the differences in these values ($\Delta\Delta H_f$ and $\Delta E_{tot.}$). This is permissible within a class of isomeric structures, when all other energy contributions of isomers are considered to be equal.

Because of this reasonably correct picture of structural aspects in the 3-membered N-homocycle **1** by MNDO, and because our interest is limited to first-order structural features, we take the MNDO level to be sufficient for calculations of qualitative features of triaziridines carrying C substituents. Caution should be exercised, however, with respect to quantities, as is shown by the following differences: *a)* MNDO calculates a difference between the lengths of the two non-equivalent N–N bonds in *c,t*-triaziridines (**1a**) while 6-31G does not. *b)* All MNDO N–N bond lengths are shorter by 0.05 Å than the 6-31G values. *c)* The sum of the MNDO bond angles around each N-atom is larger by 6–7° than the corresponding sum of the 6-31G values. These differences are due to an underestimation of lone-pair/lone-pair interactions at the MNDO level, which favor more planar arrangements at the N-atoms (*cf.* MNDO calculations of hydrazine [12]).

4. MNDO Results on the Formyltriaziridines 2 and 3. – Some selected results of our MNDO calculations on the three stereoisomers **a**, **b**, and **c** of each of **2** and **3** are listed in

Table 2. *Selected N–N Bond lengths, Bond Angles around N-Atoms, O(5)–C(4)–N(1)–N(2) Torsion Angles in, and Enthalpies of Formation of,* t,c-, c,t-, *and* c,c-*1-Formyltriaziridine* (**2a–2c**) *and* t,c-, c,t-, *and* c,c-*1-Formyl-2,3-diisopropyltriaziridine* (**3a–3c**), *as Calculated at the MNDO Level*

Bonds and bond angles[a]	**2a**[b]	**2b**	**2c**[b]	**3a**[b]	**3b**	**3c**
Bond	*Length* [Å]					
N(1)–N(2)	1.405	1.398	1.409	1.403	1.395	1.402
N(1)–N(3)	1.405	1.408	1.408	1.404	1.403	1.397
N(2)–N(3)	1.403	1.408	1.404	1.405	1.416	1.412
N(1)–C(=O)	1.467	1.466	1.474	1.468	1.464	1.458
N(2)–R	1.032	1.030	1.035	1.502	1.503	1.506
N(3)–R	1.030	1.028	1.034	1.501	1.503	1.503
Bond angle	*Angle size* [°]					
N(2)–N(1)–N(3)	59.9	60.2	59.8	60.1	60.8	60.6
C(=O)–N(1)–N(2)	119.4	125.5	123.1	118.9	126.6	127.1
C(=O)–N(1)–N(3)	118.1	117.8	124.4	117.2	120.4	131.5
N(1)–N(2)–N(3)	60.0	60.2	60.1	60.0	59.9	59.5
R–N(2)–N(1)	111.5	117.1	115.3	118.5	123.8	123.1
R–N(2)–N(3)	116.4	111.5	115.0	126.4	118.0	126.6
N(1)–N(3)–N(2)	60.1	59.6	60.1	60.0	59.3	59.9
R–N(3)–N(1)	110.9	112.1	116.3	118.4	117.9	126.2
R–N(3)–N(2)	116.4	112.2	115.3	126.8	117.1	127.7
Pyramidality	*Sum of angle sizes* [°]					
at N(1)	297.4	303.5	307.3	296.2	307.8	319.2
at N(2)	287.9	288.8	290.4	304.9	301.7	309.2
at N(3)	287.4	283.9	291.7	305.2	294.3	313.8
Torsion angle θ	*Torsion angle size* [°]					
O(5)–C(4)–N(1)–N(2)	−53.8	−31.9	+15.0	−56.3[c]	+112.0	−36.4
Enthalpy of formation [kJ/mol]						
ΔH_f	179.5	178.6	235.2	140.0	138.5	216.0

[a] R=H in **2a–2c**; R=*C* $(CH_3)_2$ in **3a–3c**.

[b] Identical values within the same column for **2a**, **2c**, and **3a** are not due to C_s symmetry since the CHO plane in the lowest-energy conformer of these compounds does not bisect the three-membered ring (see O(5)–C(4)–N(1)–N(2) torsion angles).

[c] The sign of the O(5)–C(4)–N(1)–N(2) torsion angle in **3a** is opposite to that reported in [1], since the enantiomer of **3a** had been used for comparison with the X-ray data obtained with **4** [5].

Table 2. The most important findings are: *a)* In all three stereoisomers of both **2** and **3**, the N-atoms have pyramidal configurations, irrespective of the type of substitution (H, alkyl, or formyl). *b)* The bond lengths and bond angles around the H-bearing N(2) and N(3) of **2** are similar to those around the N-atoms of the parent triaziridines **1** (see *Chapt. 3*). The i-Pr-bearing N(2) and N(3) of **3** are somewhat more flattened than the N-atoms in **1**. This effect, which is more pronounced in **3a** and **3c** with their *cis*-related i-Pr groups, may be due to steric bulk of the *N*-substituents; the relatively large (i-Pr)-N(2)–N(3) and (i-Pr)-N(3)–N(2) bond angles of about 127° in **3a** and **3c** point in the same direction. *c)* The formyl-bearing N(1) atoms of **2** and **3** are also more flattened than the N-atoms in **1**. Aside from the bulk of the formyl group, this is caused by some delocalization of the lone pair at N(1) into the carbonyl π system. This delocalization can only be weak since the MNDO N(1)–C bond lengths in **2** and **3** (*ca.* 1.47 Å) are similar to the experimentally found lengths of saturated N–C bonds (1.47 Å [13]) and also similar to the MNDO N–C bond length in CH_3NH_2 (1.460 Å [12]), but significantly longer than the experimental (1.32 Å [14]) and the MNDO (1.408 Å [12]) amide N–C bond length in formamide. *d)* The same delocalization causes the CHO plane in all six examples **2a–c** and **3a–c** to be twisted away from a position bisecting the three-membered ring, *i.e.* the O(5)–C(4)–N(1)–N(2) torsion angle θ always differs from +30° and from –150° (see the *Figure*).

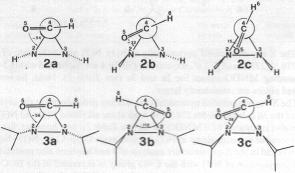
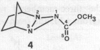


Fig. *Illustration of the O(5)–C(4)–N(1)–N(2) torsion angles θ in the formyltriaziridines* **2a–c** *and* **3a–c**

In all cases, the absolute value of the torsion angle θ is such that the formyl-O-atom lies closer to a N-atom than the formyl-H-atom. In the two *t,c*-examples **2a** and **3a**, θ is about –55°, which means that the nature of the substituents at N(2) and N(3) (H or alkyl) does not influence θ, probably because these substituents are both *trans* to the formyl group. When one of the substituents or both of them at N(2) and N(3) are *cis* to the formyl group, as in **2b**, **3b**, **2c**, and **3c**, θ varies considerably. The *cis*-oriented H-atoms at these positions, as in **2b** and **2c**, appear to attract the formyl O-atom, since in **2b** (*H*–N(2) *cis* to formyl) $\theta = -32°$ meaning that the O-atom is closer to N(2) than in **2a** (both *H*–N *trans* to formyl) and in **2c** (both *H*–N *cis* to formyl) $\theta = 15°$, *i.e.* the O-atom is placed even between the two H-atoms. In contrast, the alkyl-substituted **3b** (i-Pr group at N(2) *cis* to formyl) has the O-atom twisted away from N(2) with its *cis*-located i-Pr group towards N(3) ($\theta = 112°$) and in **3c** (both i-Pr groups *cis* to formyl) $\theta = -36°$, meaning that the O-atom is not over the ring (as it is in **2c**). *e)* As expected from considerations of bulk repulsion between *cis*-oriented substituents on three-membered rings the order of MNDO-calculated enthalpies of formation ΔH_f is *t,c* (**a** series) ≈ *c,t* (**b** series) < *c,c* (**c** series).

5. Comparison of MNDO Results on 2 and 3 with Experimental Properties. – The above MNDO-calculated features of the formyltriaziridines **2a–c** and **3a–c** qualitatively agree with the following experimentally observed properties of triaziridinecarboxylates **IIa** (R=*O*-alkyl).

a) The pyramidal configurations of the triaziridine N-atoms, irrespective of their substituents (alkyl or alkoxycarbonyl), as found by a X-ray structure analysis of the methyl *t,c*-2,3-dialkyl-triaziridine-1-carboxylate **4** [5] and as deduced from the temperature-dependent NMR phenomena of the *c,t*-2,3-dialkyl-triaziridine-1-carboxylates **5** (see *Chapt. 6*) [4], are pictured correctly by the MNDO results (see *Table 2*).



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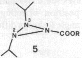
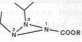


5



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R = CH_3 or C_2H_5

b) The X-ray-determined pyramidality at N(1), N(2) and N(3) (sum of the N-bond angles 278.5°, 273.9° and 272.6°, respectively [5]) for **4** are duplicated within 5–11% by the corresponding MNDO values for **2a** and **3a** (see *Table 2*). Note, however, that the calculated angles are consistently larger.

c) The X-ray-determined pyramidality in **4** is less pronounced at the acylated N(1) in **4** (sum of the N(1)-bond angles 278.5° [5]) than at the alkylated N(2) and N(3) (see above) [5], as is also calculated with MNDO for **2a** (see *Table 2*), not, however, for **3a**.

d) A twist of the ester group at N(1) (torsion angle O(5)–C(4)–N(1)–N(2) of 36° [5]) has been found in the X-ray structure analysis of **4** and has been also postulated for **5** and **6** (weak conjugation of N(1) with the C=O group as expressed in the IR C=O band [1] [4]). In the same manner, as calculated by MNDO for **2a–c** and **3a–c**, the O(5)–C(4)–N(1)–N(2) torsion in **4** is such that the C=O O-atom approaches the triaziridine ring atoms more closely than the other substituent at C(4) (CH_3O in **4**, H in **2** and **3**).

e) MNDO calculates slightly lower ΔH_f for the *c,t*-isomers **2b** and **3b**, as compared to that of the *t,c*-isomers **2a** and **3a**. This may be reflected in the slightly greater thermal stability of the *c,t*-2,3-diisopropyltriaziridines **5** as compared to their *t,c*-stereoisomers **6** [1].

6. Internal Dynamics of Formyltriaziridines. – ^1H- and ^{13}C-NMR studies of the *c,t*-triaziridinecarboxylates **5** [4] indicate non-isochronicity [15] of the geminal substituents at the prochiral centres attached to the three-membered ring, *i.e.* of the two CH_3 groups at each of the i-Pr residues of **5** and of the two H-atoms at the CH_2 group in the CH_3CH_2OCO residue of **5** ($R = C_2H_5$). The two i-Pr residues of **5** are NMR-isochronous at room temperature. These observations indicate pyramidal stability, and a *trans*-arrangement of the substituents, at N(2) and N(3) of the triaziridine ring in **5**, as well as dynamic conical symmetry of the COOR group around a line through N(1) lying in the plane of, and bisecting, the three-membered ring. At low temperature, the two i-Pr groups of **5** become NMR-non-isochronous [4] due to loss of the dynamic conical symmetry of the COOR group. The energy barrier for this dynamic effect at N(1) has been estimated [4] as 62 kJ/mol. At that time, this dynamic effect could be assigned either to the pyramidal inversion at N(1) (if the rotation around N(1)–C(4) was fast) or to the rotation around N(1)–C(4) (if N(1) was planar or pyramidal with rapid inversion). Our preference of the first-mentioned alternative [4] has so far rested solely on the IR C=O band at 1750 cm^{-1}, indicating little amide delocalization and thus suggesting rapid N(1)–C(4) rotation as well as some pyramidality at N(1).

To test our choice between these two explanations of the dynamic effect in **5**, we performed MNDO calculations on both possible processes, *i.e.* rotation around the N(1)–C(4) bond (simply called rotation) and inversion at the triaziridine N-atoms (called inversion). The results for the CHO-bearing N(1) of **2a–c** and **3a–b** and of the H-bearing N(2) (or N(3)) of **2a** are collected in *Table 3*. They show: *a)* All barriers to rotation are much lower than those to inversion. *b)* The rotation barrier is lower for the *t,c*-stereoisomers (**a** series) than for the *c,t*- and the *c,c*-stereoisomers (**b** and **c** series). *c)* In **2a**, the inversion barrier is much lower for the CHO-bearing N(1) than for the H-bearing N(2) or N(3). *d)* The inversion barrier at N(2) or N(3) of **2a** is 136 kJ/mol, a value close to the 3-21G value at N(3) in the unsubstituted triaziridine **1a** (137 kJ/mol [2]). *e)* In **3b**, the model structure most similar to the experimentally examined compounds **5b**, the rate-determining dynamic process at N(1) is the inversion, since its barrier is more than 5 times higher than that of rotation. *f)* The inversion barrier at N(1) in **3b** is 53 kJ/mol, a value close to the experimentally determined value (by ^{1}H-NMR coalescence 62 kJ/mol [4]) for the dynamic process in **5** (R = C_2H_5).

Table 3. *Barriers to Inversion at N(2) of* **2a** *and at N(1) of* **2a**, **2b**, **3a**, *and* **3b**, *and to Rotation around the N(1)–C(4) Bond of* **2a** *to* **2c**, *and* **3a**, *to* **3b**, *as Calculated by MNDO*

Compound	N-Atom involved	Substituent at N-Atom	Bond involved	Dynamic process	Barrier to process [kJ/mol]
2a	N(2) or N(3)	H	–	inversion	136
2a	N(1)	CHO	–	inversion	92
2b	N(1)	CHO	–	inversion	64
2c	N(1)	CHO	–	inversion	not calculated
3a	N(1)	CHO	–	inversion	88
3b	N(1)	CHO	–	inversion	53
2a	–	CHO	N(1)–C(4)	rotation	9
2b	–	CHO	N(1)–C(4)	rotation	19
2c	–	CHO	N(1)–C(4)	rotation	23
3a	–	CHO	N(1)–C(4)	rotation	7
3b	–	CHO	N(1)–C(4)	rotation	17

7. Conclusions. – The present MNDO calculations support our previously developed intuitive point of view that certain aspects of triaziridine chemistry are closely connected to each other, namely the pronounced pyramidality at its N-atoms, the high resistance to inversion at its N-atoms, the non-coplanarity of amide substructures involving its N-atoms, and the low resistance to rotation around its amide N–C(=O) bonds. All these aspects are due to the strong tendency of electron localization at the triaziridine N-atoms and the lower tendency towards π delocalization to attached C=O groups. While the latter tendency is not strong enough to achieve coplanarity and thus impede the rotation at the N–C(=O) bond, it can nevertheless lower the barrier to inversion at these amide-type N-atoms.

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