Opening the aziridinimine ring: a theoretical study

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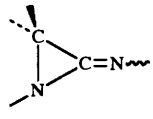
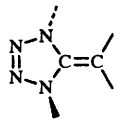
The opening of a model aziridinimine has been studied by *ab initio* molecular orbital methods. Geometries of stationary points were optimized at the MP2/6-31G(d,p) level, while relative energies were estimated using configuration interaction (CISDQ) and quadratic configuration interaction [QCISD(T)] methods with the 6-311G(d,p) basis set and corrected for zero-point energies. The [2 + 1] cycloreversion of aziridinimine giving an imine plus an isocyanide is consistently favoured over its isomerization yielding other alternative rings. The calculated enthalpy of activation for cycloreversion of the unsubstituted molecule amounts to $\Delta H^{\ddagger}$ = 150 kJ mol^{-1} at 0 K. While methyl substitution at the exocyclic nitrogen activates this fragmentation, methyl substitution at the ring nitrogen atom slightly deactivates it. For trimethylaziridinimine, we estimate a value of $\Delta H^{\ddagger}$ = 120 kJ mol^{-1}. While the latter can be compared with the experimental values of 112–128 kJ mol^{-1} measured for alkyl substituted species, the entropy of activation for alkylated aziridinimines is calculated to be positive, $\Delta S^{\ddagger}$ (calc) ≃ 10 J mol^{-1} K^{-1}, in conflict with available experimental results, $\Delta S^{\ddagger}$ (exptl) = −13 to −24 J mol^{-1} K^{-1}. The energy barrier for ring–ring rearrangement giving an alternative ring with an exocyclic C=C bond amounts to *ca.* 160–170 kJ mol^{-1}. The stereochemistry of the [2 + 1] cycloreversion can be rationalized by a stereoelectronic effect. Protonation occurs at the exocyclic nitrogen. The aziridinimine radical cation ion still has a cyclic structure; the adiabatic ionization energy is estimated to be $E_{i.a}$ (aziridinimine) = 9.4 ± 0.3 eV. The cyclic ion easily undergoes ring-opening yielding a more stable open distonic radical cation, $H_2C^{\cdot}$–NH–C≡NH^{+}, which lies 128 kJ mol^{-1} below the cyclic ion.

Introduction

Aziridinimines **I** belong to the class of heteroatomic analogues



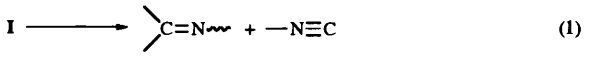
I



II

of methylenecyclopropanes[1] whose chemistry continues to attract much attention, in part owing to their great utility as starting materials in heterocyclic synthesis.

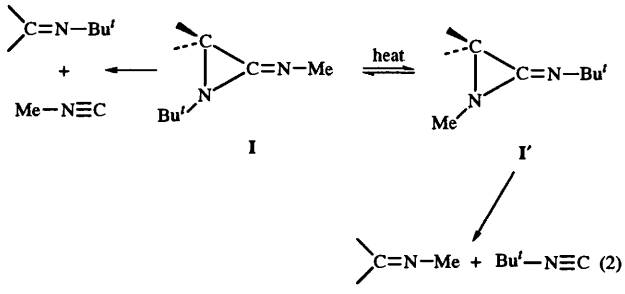
Quast and Schmitt[2] reported the first preparation of a derivative of **I** by chlorination of a tri-*tert*-butylguanidine. The synthetic procedure has subsequently been modified so that the method is not confined only to the presence of bulky substituents.[3] More recently, **I** has been obtained by photochemical[4] or thermal[5] elimination of molecular nitrogen from alkylidene-tetrazoles **II**. Submitted to photolysis[4] or thermolysis,[5] **I** has been shown to undergo a cheletropic reaction giving an imine plus an isocyanide [reaction (1)].



(1)

An interesting mechanistic feature of this process is that in some cases thermolysis leads to a mixture of imine and isocyanide fragments whose existence apparently arises from a valence isomerization **I** ⇌ **I'** prior to the cheletropic reaction [eqn. (2)].

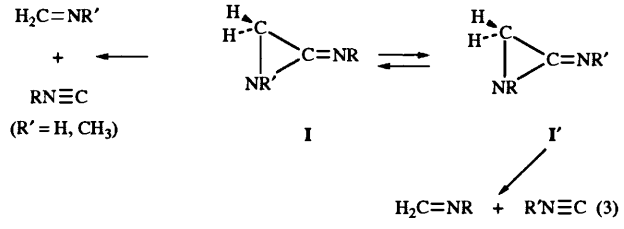
With regards to the cycloreversion, Quast *et al.*[6] were recently able to determine the activation parameters of the thermolysis of a series of aziridinimines [reaction (1)]. Accordingly, the enthalpy variation of activation $\Delta H^{\ddagger}$ varies from 112 to 128 kJ mol^{-1}, whereas the variation in the entropy of activation, $\Delta S^{\ddagger}$, is surprisingly negative, ranging from −13 to −24 J mol^{-1} K^{-1}. There has been no other quantitative



(2)

information on the competition between both cycloreversion and isomerization reactions described in reaction (2).

As part of our continuing theoretical study of the structures and reactivities of heteroderivatives of cyclopropanimine[7–9] we have carried out *ab initio* molecular orbital calculations on the simplest model system [reaction (3)]. We have been particularly



(3)

interested in the detailed mechanism of the considered reactions as well as in the related activation parameters. The substituent effect on the cycloreversion has also been probed by calculations on the systems containing a methyl group. To extend the scope of the study, we have also examined the protonation and the process following ionization of aziridinimine.

Calculations

All *ab initio* MO calculations were carried out using a local

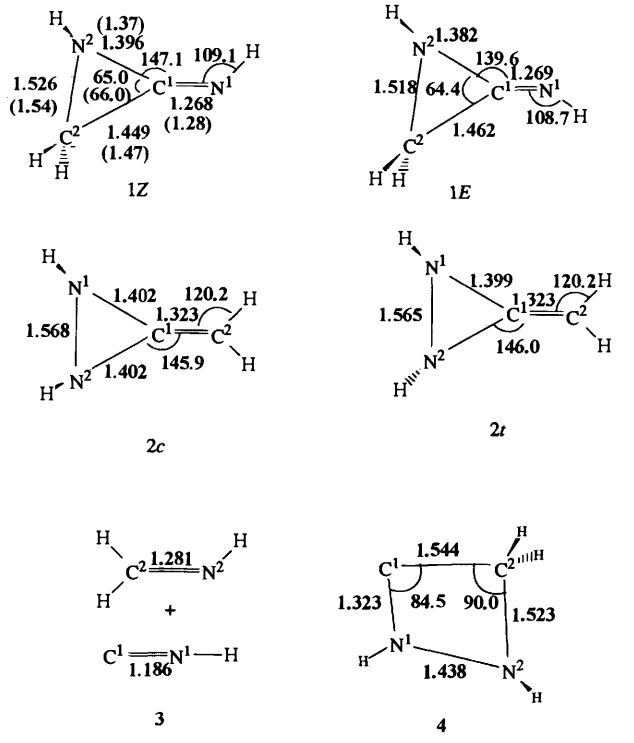


Fig. 1 Selected MP2/6-31G(d,p) geometrical parameters of $[C_2H_4N_2]$ equilibrium structures. For **1Z**, values given in parentheses are those determined from the crystal structure of a spiroaziridinimine (ref. 11).

version of the GAUSSIAN 92 set of programs.[10] The stationary points were first located using Hartree–Fock (HF) wavefunctions with the dp-polarized 6-31G(d,p) basis set and characterized at this level by harmonic vibrational analysis. The identity of each transition structure has been determined by intrinsic reaction coordinate (IRC) calculations. Geometrical parameters of the equilibrium and transition structures of interest were then refined using second-order Møller-Plesset perturbation theory calculation [MP2/6-31G(d,p)]. Finally, thermochemical parameters were estimated using electronic energies computed by the configuration interaction (CISDQ) and quadratic configuration interaction [QCISD(T)] methods with the larger 6-311G(d,p) basis set at MP2-optimized geometries and corrected for zero-point vibrational energies. For the ionized structures, the unrestricted formalism (UHF, UMP2, UCI) has been applied. Throughout this paper, bond lengths are given in angströms, bond angles in degrees, total energies in hartrees, zero-point and relative energies in kJ mol^{-1}.†

Results and discussion

Selected geometrical parameters obtained from MP2/6-31G(d,p) optimizations for the equilibrium and transition structures of the unsubstituted $(C_2H_4N_2)$ system are displayed in Figs. 1 and 2. By convention, we will designate a transition structure (TS) linking both equilibrium structures *X* and *Y* by *X*/*Y*. Corresponding total, zero-point vibrational and relative energies calculated at different levels are summarized in Table 1. Unless otherwise noted, the energetics quoted hereafter correspond to the values obtained from QCISD(T)/6-311G(d,p) + ZPE calculations.

Aziridinimine and isomers

The unsubstituted aziridinimine **1** can exist in two distinct conformations **1*Z*** and **1*E***. Both conformers are calculated to have a similar energy content. The energy barrier for *E*–*Z* interconversion through the transition state (TS) for nitrogen

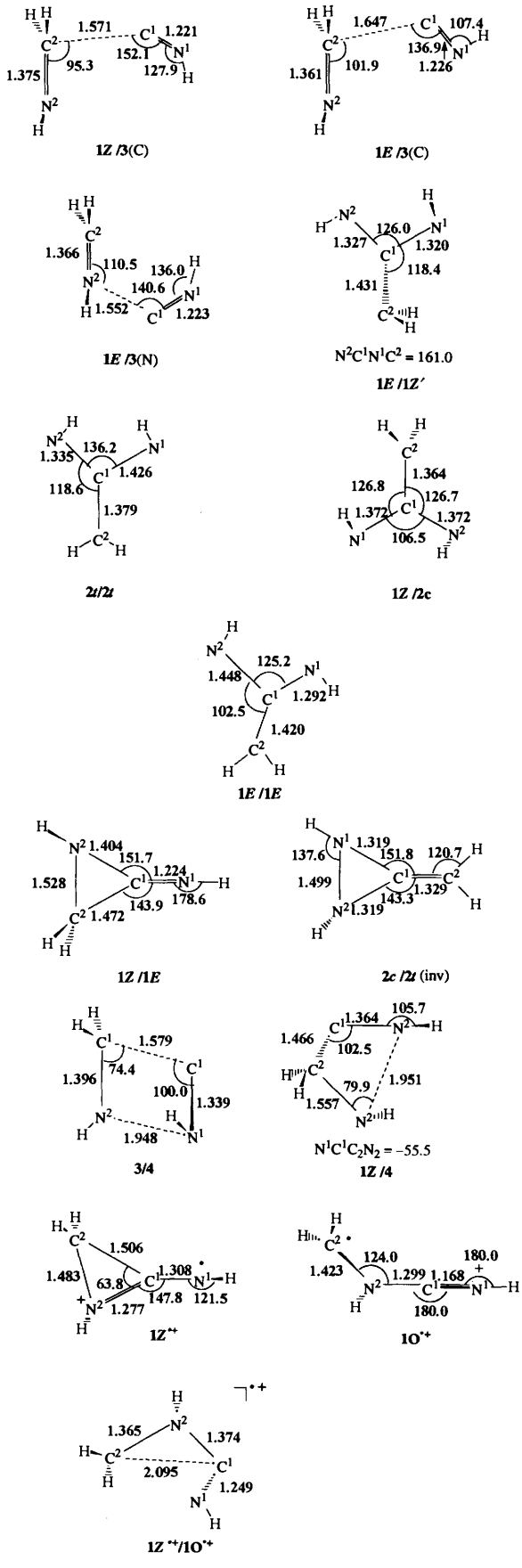


Fig. 2 Selected MP2/6-31G(d,p) geometrical parameters of the transition structures for isomerizations and cycloreversions of aziridinimine and the ionized structures

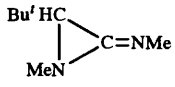
† 1 Hartree = 4.360×10^{-18} J.

Table 1 Total and relative energies of the $[C_2N_2H_4]$ system at different levels of theory

Molecules[a]	Total energies[b]/Hartrees				Relative energies[c]/kJ mol^{-1}		
	MP2	CISDQ	QCISD (T)	ZPE[d]	MP2	CISDQ	QCISD (T)
1*Z*	−187.555 74	−187.582 78	−187.608 54	161.1	0.0	0.0	0.0
1*E*	−187.555 89	−187.588 01	−187.608 59	161.3	−0.2	13.9	0.2
2*c*	−187.509 07	−187.538 69	−187.564 76	159.8	121.2	114.4	113.7
2*t*	−187.518 33	−187.547 60	−187.573 61	160.9	98.0	92.2	91.5
3	−187.545 60	−187.578 90	−187.605 64	139.1	4.6	−11.8	−14.4
4	−187.472 78	−187.508 11	−187.533 56	162.7	219.4	197.6	198.2
1*Z*/1*E*	−187.512 39	−187.537 84	−187.563 75	154.1	105.2	111.0	110.6
1*Z*/1*Z*(inv)	−187.541 88	−187.567 43	−187.593 15	149.1	25.2	28.9	28.8
2*c*/2*t*	−187.477 09	−187.505 61	−187.531 25	155.2	200.4	196.7	197.0
1*Z*/3(C)	−187.488 88	−187.512 53	−187.547 64	151.0	165.4	174.3	149.8
1*E*/3(C)	−187.486 74	−187.510 00	−187.546 16	150.1	170.2	181.1	152.8
1*E*/3(N)	−187.459 84	−187.480 14	−187.521 27	146.6	236.2	245.0	214.6
1*E*/1*Z*′	−187.468 43	−187.489 75	−187.530 45	148.7	216.8	231.8	192.5
1*E*/1*E*	−187.460 21	−187.483 46	−187.533 20	150.8	240.5	250.4	187.5
2*t*/2*t*	−187.462 03	−187.484 45	−187.528 21	149.7	236.6	246.7	199.3
1*Z*/2*c*	−187.420 55	−187.491 51	−187.533 49	148.5	332.4	224.5	184.5
3/4	−187.392 52	−187.423 46	−187.454 20	163.0	430.4	420.2	407.1
1*Z*/4	−187.322 70	−187.420 74	−187.451 97	163.0	613.7	427.4	413.0

[a] Based on MP2/6-31G(d,p) geometries given in Figs. 1 and 2. The TS **1*Z*/1*Z*** for nitrogen inversion is not given in Fig. 1. [b] With the 6-311G(d,p) basis set; core orbitals are frozen. [c] Including zero-point energies. [d] Zero-point energies from HF/6-31G(d,p) calculations scaled by a factor 0.9.

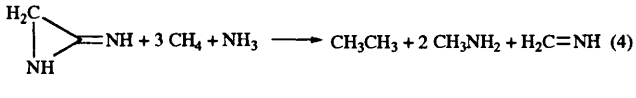
inversion **1*Z*/1*E*** is calculated to be 111 kJ mol^{-1}. Experimentally,[6] the ratio of both stereoisomers *E* and *Z* of the substituted molecule **1a** at room temperature has been established to be *ca.* 57:43 and the Gibbs' energy of activation for methyl inversion was estimated to be $\Delta G^{\ddagger} = 98$ kJ mol^{-1}.



1a

The crystal structure of a spiroaziridinimine having a *Z* conformation has been determined;[11] for the sake of comparison, its experimental parameters have also been given in Fig. 1 (structure **1*Z***). The barrier height for nitrogen inversion within the ring *via* TS **1*Z*/1*Z*** amounts to 29 kJ mol^{-1} and is of the same order of magnitude as that of nitrogen inversion in phosphaaziridine.[9] The alternative structure, alkylidenediaziridine **2**, featuring an exocyclic C=C double bond is consistently higher in energy than **1**. The *trans* conformer **2*t*** is, as expected, 22 kJ mol^{-1} more stable than the *cis*-**2*c***, but **2*t*** still lies 92 kJ mol^{-1} above **1*Z***. Both conformers of **2** are connected by TS **2*c*/2*t*** with an energy barrier of 83 kJ mol^{-1} relative to **2*c***. The latter is much larger than the corresponding barrier in **1*Z*** mentioned above; this is no doubt due to the existing lone pair repulsion within the ring that apparently destabilizes the corresponding TS. The C=N stretching wavenumbers[12] in both aziridinimines **1*E*** and **1*Z*** are estimated to be centred at 1798 cm^{-1}, a value comparable to the observed IR absorption at 1805 cm^{-1} of the substituted **1a**. Note that the corresponding values in methanimine and cyclopropanimine are 1640 and 1780 cm^{-1}, respectively.[7] The high vibrational wavenumber in **1** relative to methanimine is again a clear manifestation of a strong coupling between both three-membered ring and C=N moiety. In connection with this point, it is of interest to estimate the ring strain in **1**. For this purpose, we have considered both isodesmic reactions (4) and (5).

The heats of reaction calculated at the MP4/6-31G(d,p)//MP2/6-31G(d,p) level amount to −23 and −56 kJ mol^{-1} for reactions (4) and (5), respectively; this clearly indicates that aziridinimine **1** exhibits a markedly smaller ring strain than aziridine. The nuclear inconvenience due to the coupling in **1** is largely compensated by an electronic advantage created by electron delocalization and stabilization.



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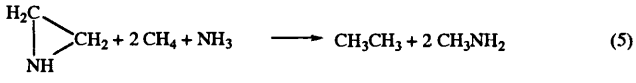


(5)

Cheletropic reaction of aziridinimine

This reaction is marginally exothermic; the fragments HN≡C + CH_2=NH **3** lie *ca.* 14 kJ mol^{-1} below **1*Z***. Three TSs shown in Fig. 2 have been characterized for this decomposition. Both structures **1*Z*/3**(C) and **1*E*/3**(C) have shorter C^1–C^2 and longer C^1–N^2 distances, whereas **1*E*/3**(N) has short C^1–N^2 and longer C^1–C^2 distances. It is clear from the energetics displayed in Fig. 3 that the cycloreversion involving a more advanced breaking of the C–N bond of the three-membered ring *via* **1*Z*/3**(C) and **1*E*/3**(C) is definitely more favoured than breaking of the C–C bond. A C–N bond is of course weaker than a C–C bond. This fact could also be understood by looking at the reverse reaction, namely the cycloaddition of HN≡C + CH_2=NH. A frontier orbital consideration suggests that the latter is mainly controlled by the HOMO (isocyanide)–LUMO (methanimine) interaction. While the HOMO of HN≡C is the carbon lone pair, the LUMO of H_2C=NH is a π* (C=N) in which the carbon exhibits a larger MO coefficient. Concerning the charge distribution, the carbon centre also bears a large positive charge. Thus, both charge and orbital criteria suggest a preferential nucleophilic attack of the isocyanide carbon on the methanimine carbon which effectively corresponds to both TS **1*Z*/3**(C) and **1*E*/3**(C) (Fig. 3). The slight preference of **1*Z*/3**(C) over **1*E*/3**(C) can be rationalized in terms of a stereoelectronic effect which consists of a circulation of the migrating electron pairs in the same direction. These migrating electron pairs will form the novel bonds of the product. For a detailed description of the effect in the analogous CH_2=PH + HN≡C system, see ref. 9.

Our best estimate suggests a classical barrier height of 150 kJ mol^{-1} for the cheletropic fragmentation of the unsubstituted aziridinimine **1**; this value should be regarded as an upper limit because it will be reduced following further extension of the basis functions and/or incorporation of multi-reference configuration interaction.

In an attempt to estimate the effect of the alkyl substituents,

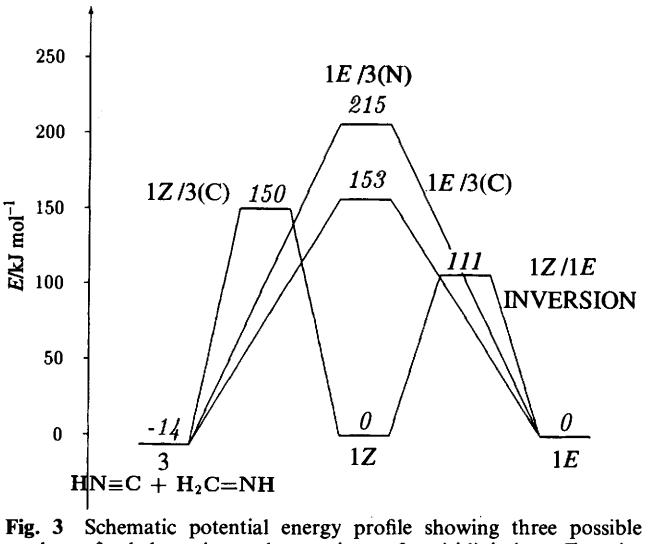


Fig. 3 Schematic potential energy profile showing three possible modes of cheletropic cycloreversion of aziridinimine. Energies obtained from QCISD(T)/6-311G(d,p) + ZPE level.

we have considered the decomposition of methylated aziridinimines. Since we are mainly interested in the relative changes of the thermochemical parameters upon methyl substitution at the three possible sites of aziridinimine, we have only performed calculations at the HF/6-31G(d,p) level which are summarized in Table 2. It is apparent that a methyl group bonding at the exocyclic nitrogen tends to reduce the barrier significantly and, in accord with the Hammond postulate, the reaction exothermicity increases. This acceleration effect is likely to arise from a larger stability of the methyl isocyanide product (CH_3–N≡C). Methyl substitution within the ring induces a much smaller effect: while an *N*-methylation marginally deactivates the cycloreversion, a *C*-methylation slightly activates it. Assuming a simple additivity of the individual actions of the substituents, the overall effect of the trimethyl substitution turns out to be largely beneficial for the cycloreversion with a decrease of *ca.* 30 kJ mol^{-1} on the barrier height relative to the unsubstituted species. Using the calculated value mentioned above for **1**, we could thus estimate an upper limit for the energy barrier of *ca.* $\Delta E^{\ddagger}$ = 120 kJ mol^{-1} for the [2 + 1] cycloreversion of trimethylaziridinimine. This value is consistent with the experimental values $\Delta H^{\ddagger}$ = 112–128 kJ mol^{-1} derived by Quast *et al.*[6] from kinetic measurements on a series of alkyl substituted molecules. With regard to the entropy of activation, we have calculated a positive variation, $\Delta S^{\ddagger}$ being *ca.* 10 J mol^{-1} K^{-1} for the substituted and unsubstituted aziridinimines considered. In contrast, Quast *et al.* derived a negative change, namely $\Delta S^{\ddagger}$ varying from −13 to −24 J mol^{-1} K^{-1}. We do not see any obvious reason for this discrepancy; it might be due to a solvent effect that we have not included in our calculations. However, we wish to note, on the one hand, that the experiments were performed in solvents of low polarity, and on the other hand, the calculated values are consistent with the fact that the geometry of aziridinimine **1** is more compact than the TS for cycloreversion **1**/**3**; most concerted fragmentation reactions have in fact positive $\Delta S^{\ddagger}$ values. In the opposite direction, the activation entropy for cycloaddition of H_2C=NH to HN≡C amounts to −115 J mol^{-1} K^{-1}.

Ring–ring rearrangement of aziridinimine

We now turn to the rearrangement of **1**. At least four relevant TS have been located and are shown in Fig. 2. All these TSs, **1*E*/1*Z*′**, **1*Z*/2*c***, **1*E*/1*E*** and **2*t*/2*t***, are characterized by an open form. Note that the notation **1*Z*′** is used to indicate that in substituted systems **1*Z*′** is not identical with **1*Z***. The planar open structure **1*E*/1*E*** represents a TS for racemization of **1*E*** and is 187 kJ mol^{-1} above **1*E***. The transition vector of its imaginary vibrational mode corresponds to a disrotatory ring-closing along the C^2–N^2 bond giving **1*E*** in both directions. This is supported by the geometrical parameters in which the C^1–N^1 bond, corresponding to the exocyclic C=N bond, has the shortest bond length. A similar TS for racemization of **1*Z*** should also exist. Both open but non-planar TS **1*Z*/2*c*** and **1*E*/1*Z*′** describe the isomerization between **2*c*** and **1*Z*** and **1*E*** and **1*Z*′**, respectively. The latter corresponds to the process illustrated in eqn. (2). The open planar structure **1*E*/1*E*** is often postulated in the literature as an intermediate for various isomerization reactions. While our numerous results suggest that it is not an energy minimum in the gas phase, a minimum character in the presence of polar solvent could not be ruled out. The non-planar TS **1*E*/1*Z*′** might play an important role in the mixed formation of the exothermic products **3**. In fact, there are two possible routes for the decomposition of a substituted aziridinimine depending on the temperature and the alkyl groups attached to nitrogens.[2] While the first route is a direct decomposition of **1*E*** into the products **3** as examined in the preceding paragraph, the second involves an initial rearrangement leading to the isomer **1*Z*′** *via* **1*E*/1*Z*′**. A subsequent decomposition of **1*Z*′** finally results in the products **3′** where the substituents are interchanged. According to the available experimental results,[2] the first route seems to dominate at lower temperatures (50 °C) and when a *tert*-butyl group is attached at the exocyclic nitrogen (Scheme 1, *b*). The isocyanide product becomes thus more stabilized in this manner, both thermodynamically and kinetically. When this bulky group is attached at the ring nitrogen, upon heating to higher temperatures (130 °C), the ring structure is likely to have enough internal energy to undergo also a ring–ring isomerization giving an aziridinimine isomer where the bulky group is now the substituent at the imine function (Scheme 1, *a*). It seems that a bulky substitution at the ring nitrogen slows down the direct cycloreversion, while at the same time the ring–ring rearrangement is accelerated. However, a recent kinetic study[6] pointed out that the latter still remains the slower step.

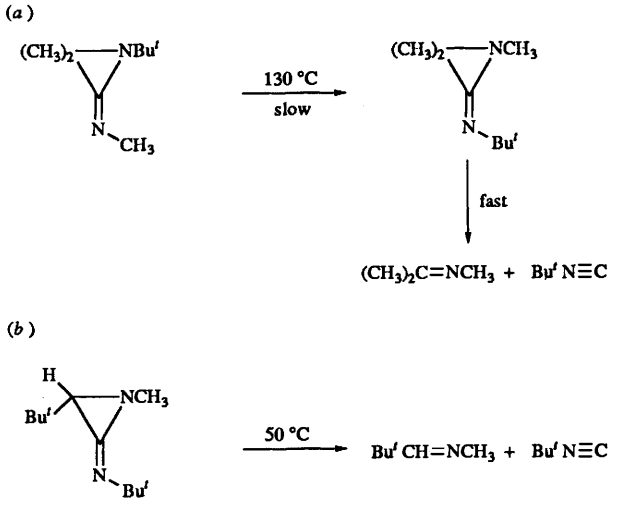
The calculated barrier for the ring–ring isomerization through **1*E*/1*Z*′** amounts to 193 kJ mol^{-1}. Owing to the zwitterionic nature of **1*E*/1*Z*′**, this barrier height is expected to be lowered significantly if multi-reference wavefunctions could be obtained.[9] Separate multi-reference calculations using the CASPT2 method suggest a reduction of *ca.* 30 kJ mol^{-1} for this barrier height. Thus, a realistic value for this barrier is *ca.* 160–170 kJ mol^{-1}, which remains somewhat larger than the barrier for a direct cycloreversion (150 kJ mol^{-1}, see above). In other words, the ring–ring isomerization apparently constitutes the slower step of the two-step rearrangement [eqn. (2)], in agreement with the experimental observations mentioned above.

Structure **1*Z*/2*c*** connecting **2*c*** with **1*Z*** lies 72 kJ mol^{-1} above **2*c*** and is 8 kJ mol^{-1} below **1*E*/1*Z*′**. Applying the above results to the photodecomposition of **II**, we could postulate that if structures **2*c*** and/or **2*t*** could be formed as the primary products, they then presumably undergo isomerization giving the more stable isomer **1**. Finally, **2*t*/2*t*** is characterized as the

Table 2 Effect of the methyl substitution on the cycloreversion of aziridinimine

State of substitution	Variation in $\Delta H^{\ddagger}$/ kJ mol^{-1} [a]	Variation in ΔH_r/ kJ mol^{-1} [a]
H(C)/H(N)/H($N_{exocycl}$)	0	0
H(C)/H(N)/CH_3($N_{exocycl}$)	−26	−11
H(C)/CH_3(N)/H($N_{exocycl}$)	2	6
CH_3(C)/H(N)/H($N_{exocycl}$)	−5	−1

[a] From HF/6-31G(d,p) energies of fully optimized structures at this level and corrected for zero-point energies.



Scheme 1

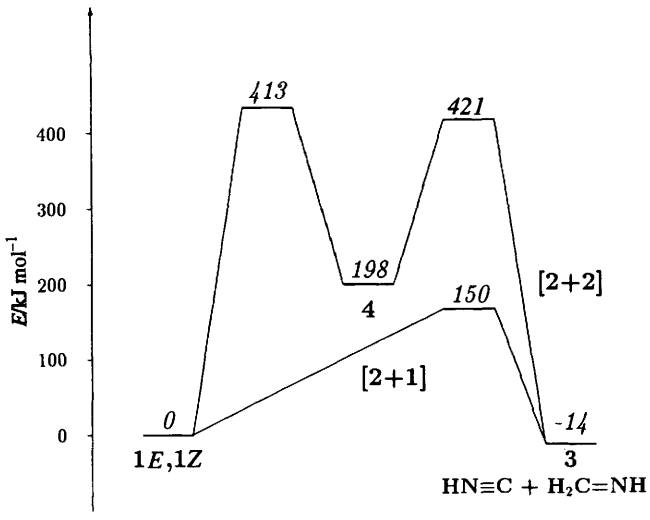


Fig. 4 Schematic potential energy profile showing both [2 + 1] and [2 + 2] cycloadditions of the HN≡C + H_2C=NH system. Values are obtained at the QCISD(T)/6-311G(d,p) + ZPE level.

TS for racemization of **2*t***; the ring is formed along the N^1–N^2 bond. During this process the exocyclic C=C bond is only marginally affected. **2*t*/2*t*** lies *ca.* 107 kJ mol^{-1} above **2*t***, thus the racemization of the latter proceeds much more easily than that of **1**.

2 + 2 Cycloaddition

On the energy potential surface drawn in Fig. 4, we have also found a four-membered ring containing a carbene moiety. Although this carbene is highly unstable (198 kJ mol^{-1} above **1*Z***) owing to additional repulsion between the nitrogen lone pairs, it can still be connected to the reaction path by two transition structures. The first one, TS **3/4**, represents the [2π + 2π] cycloaddition of isocyanide to methanimine with an advanced formation of the C–C bond. This reaction follows a suprafacial–antarafacial approach in accord with frontier orbital considerations. Nevertheless, **3/4** lies 421 kJ mol^{-1} higher than the reactants **3**. Earlier calculations [8,9] for this type of four-membered heterocyclic carbenes reveal that they could be stabilized by elements which do not have lone pairs owing to the loss of electron repulsion. The second TS **1*Z*/4** is associated with the rearrangement of aziridinimine **1*Z*** to carbene **4** with an energy barrier of 413 kJ mol^{-1} relative to **1*Z***. Starting from **1*Z*** this process is apparently induced by a cleavage of the σ(C^1–N^2) bond and followed by an out-of-plane motion of the CNH moiety giving a bicyclic structure in order to form a novel chemical σ(N^1–N^2) bond. Because of its high thermodynamical instability, we can, however, conclude that **4** is not involved as an intermediate in the reaction path.

Protonation at the imino and ring nitrogen atoms of aziridinimine

In this section we discuss a particular aspect of the reactivity of aziridinimine by considering the protonation at the nitrogen. The calculated proton affinities (PA) included in Table 3 show that protonation is more favourable if it occurs at the imino nitrogen. The relative protonation energies also listed in Table 3 are the computed energies of the following proton transfer reactions.

Table 3 Calculated proton affinities of nitrogen (PA/kJ mol^{-1}) at the HF/6-31G(d,p) + ZPE level

Molecules[a]	PA/kJ mol^{-1}	ΔPA[b]/kJ mol^{-1}
N_{ring} **1**	886	−5
$N_{exocycl}$ **1**	957	−51
NH_3	881	
H_2C=NH	906	
Aziridine	947	

[a] Based on fully optimized HF/6-31 G(d,p) geometries. [b] Differences in PAs, see text.

The negative values in both reactions (6) and (7) indicate a certain increase in basicity relative to methanimine and ammonia. Nevertheless, the very low exothermicity of −5 kJ mol^{-1} of reaction (7) implies that the basicity of the sp^3 hybridized nitrogen atom is comparable for both ammonia and aziridinimine molecules. To check whether the ring nitrogen atom is influenced by the imino moiety, we have compared the PA of **1** with that of aziridine. The latter has a much larger nucleophilic nitrogen centre; its PA value amounts to 947 kJ mol^{-1} (see also ref. 13). Thus, the PA of nitrogen in aziridine is much larger than that of its counterpart in ammonia (by 66 kJ mol^{-1}); this is mainly due to the donation of two alkyl groups. However, this positive effect is virtually neutralized by that of the exocyclic imine function in aziridinimine as evidenced by the small heat of reaction (7). The larger calculated heat of reaction (6), −51 kJ mol^{-1}, also shows that substitution at carbon in CH_2=NH by a ring structure also increases the basicity of the imino nitrogen. This phenomenon, which is due to a better charge stabilization through resonance of the protonated species, is similar to methyl and amino substituents. This result supports the proposition that the imino group acts as an electron-withdrawing group and electron delocalization from the ring into the imino group in general results in a larger proton affinity.

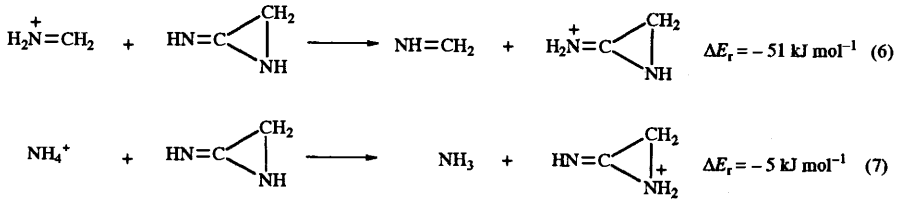


Table 4 Vertical and adiabatic ionization energies for the aziridinimine molecule at different levels of theory

Molecules[a]	Total energies[b]/Hartrees				Relative energies[c]/eV		
	MP2	CISDQ	QCISD(T)	ZPE[d]	MP2	CISDQ	QCISD(T)
1Z	−187.555 74	−187.582 78	−187.608 54	161	0.0	0.0	0.0
$\mathbf{1Z}^{\bullet+}(IE_{i,a})$	−187.214 19	−187.250 10	−187.274 19	163	9.2	9.0	9.1
$\mathbf{1Z}^{\bullet+}(IE_{i,v})$	−187.113 06	−187.220 38	−187.255 11	161	12.0	9.8	9.6
$\mathbf{1O}^{\bullet+}$	−187.265 14	−187.293 35	−187.317 37	148	7.9	7.7	7.8
$\mathbf{1Z}^{\bullet+}/\mathbf{1O}^{\bullet+}$	−187.125 97	−187.222 89	−187.253 14	147	11.5	8.9	9.5

[a] Based on UMP2/6-31G(d,p) geometries given in Figs. 1 and 2. [b] With the 6-311G(d,p) basis set; core orbitals are frozen. [c] Including zero-point energies. [d] Zero-point energies from HF/6-31G(d,p) calculations and sealed by a factor 0.9.

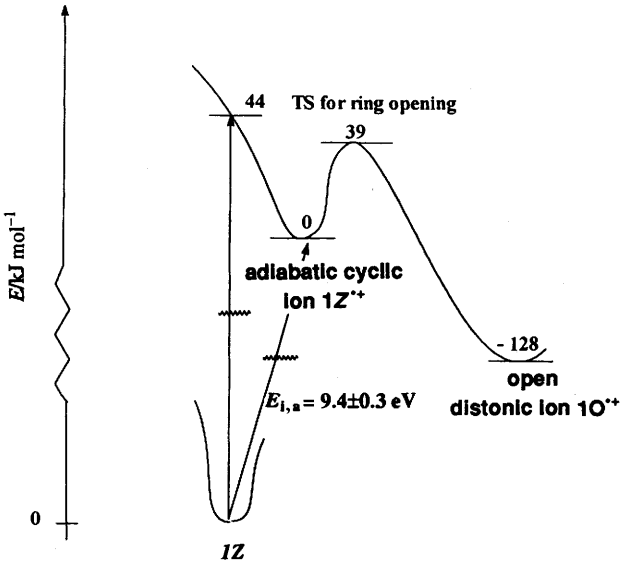


Fig. 5 Schematic potential energy surface showing the ionization of aziridinimine. Energies are obtained from QCISD(T)/6-311G(d,p) + ZPE calculations. $E_{i,a}$ is a corrected value, see text.

Ionization of aziridinimine

To obtain an insight into the electronic structure of **1**, we have also examined its radical cation. Calculated total energies and first ionization energies are listed in Table 4. The UMP2/6-31G-(d,p) geometrical parameters of the ionized structures $\mathbf{1Z}^{\bullet+}$, $\mathbf{1O}^{\bullet+}$ and $\mathbf{1Z}^{\bullet+}/\mathbf{1O}^{\bullet+}$ are presented in Fig. 2, while a schematic energy profile obtained at the QCISD(T)/6-311G(d,p) + ZPE level is illustrated in Fig. 5. Comparison of both vertical and adiabatic ionization energies of **1Z** reveals a moderate stabilization ($\Delta E_{i,a}$ = 0.5 eV) resulting from a geometry relaxation in the strained three-membered ring system. Indeed, the equilibrium ionic structure remains cyclic. The HOMO of aziridinimine extends over the whole molecular skeleton with the largest component on the exocyclic nitrogen. By way of simplification, it could be seen as the lone pair orbital of the latter. Therefore, removal of one electron from this pair leads to a nitrogen-centred radical. While the radical site is located at the imino group, the positive charge extends over the ring frame. Inspection of the geometry of the radical ion $\mathbf{1Z}^{\bullet+}$ emphasizes that the ring nitrogen lone pair orbital does not really participate in the ionization process as such, but instead it delocalizes into the empty p orbital of the central carbon to form a new bond as evidenced by the shortened carbon–nitrogen distance (1.27 Å) which is essentially that of a double C=N bond. In turn, the exocyclic C–N bond elongates (1.308 Å) and rotates. Although the relative separation of both radical and positive charge sites in $\mathbf{1Z}^{\bullet+}$ confers on it a certain distonic radical cation character, it is not the most stable ionized form. As expected, the ring $\mathbf{1Z}^{\bullet+}$ does open *via* a homolytic cleavage of the σ(C–C) bond which is presumably the weakest bond. An energy barrier of 39 kJ mol^{-1} separates $\mathbf{1Z}^{\bullet+}$ from the more stable open ion $\mathbf{1O}^{\bullet+}$. The corresponding TS $\mathbf{1Z}^{\bullet+}/\mathbf{1O}^{\bullet+}$ clearly shows the ring cleavage process in which the C–C distance is markedly elongated up to 2.095 Å. Together with geometrical adjustments, the charge distribution is completely reorganized in $\mathbf{1O}^{\bullet+}$ which is in fact a distonic radical ion. This can be easily understood in terms of electron delocalization. A new π ($C_1{\equiv}N_1$) bond is formed following a σ(C^1–C^2) cleavage. This process is followed by a delocalization of the perpendicular N^1 lone pair into the empty pπ (C^1) orbital which is formed at the TS. The radical site now becomes part of the terminal CH_2 group. Such charge and geometry reorganization taking place in $\mathbf{1O}^{\bullet+}$ is also substantiated by its geometrical parameters: $r(C^1$–$N^1)$ = 1.168 Å, $r(C^1$–$N^2)$ = 1.299 Å, C^1–$\widehat{N^1}$–H = 180.0° and N^1–$\widehat{C^1}$–N^2 = 180.0°. The linearity reveals that the positive charge is thus spread over the nitrilium moiety (H–N≡C–$^+$) which is much more stabilized. Overall, the cation $\mathbf{1O}^{\bullet+}$ is calculated to be more stable than the closed form $\mathbf{1Z}^{\bullet+}$ by 128 kJ mol^{-1}. An important fact is that the energy of the TS $\mathbf{1Z}^{\bullet+}/\mathbf{1O}^{\bullet+}$ is slightly lower than that of the vertically ionized structure of **1Z** (by 5 kJ mol^{-1}). This implies that ionized aziridinimine generated in its σ ground state possesses enough critical energy to rearrange yielding the distonic ion $\mathbf{1O}^{\bullet+}$. In other words, the rearranging ion $\mathbf{1O}^{\bullet+}$ is likely to be produced together with ionized aziridinimine, *e.g.* in a chemical ionization mass spectrometric experiment. The first band of the photoelectron spectrum of aziridinimine is also expected to be quite broad. It is known that ionization energies are usually underestimated at the level of theory employed here by *ca.* 0.3 eV; we could therefore suggest a value, $E_{i,a}$ (aziridinimine) = 9.4 ± 0.3 eV. Experiments using mass or photoelectron spectrometry are clearly desirable to clarify the situation regarding the distonic ion.

Summary

We have constructed the potential energy surface of aziridinimine **1Z**, **1E** leading to its fragment products CH_2=NH + HN≡C *via* a cheletropic decomposition of the ring system or *via* a primary ring isomerization followed by a cycloreversion. The cheletropic reaction gives rise to three possible transition-state structures from which **1Z**/**3**(C) corresponding to a CC approach in which a *syn* position is energetically the most favourable. Methyl substitution at the exocyclic nitrogen activates the cycloreversion, whereas methyl substitution at the exocyclic nitrogen deactivates the same process. Isomerization of aziridinimine yielding an alternative ring with an exocyclic C=C bond **2** is also possible *via* an open TS, but this reaction is more energy-demanding than direct cycloreversion. Aziridinimine **1Z** is the end-product of the photodecomposition of a five-membered ring **II**. We postulate that during this reaction, methyleneaziridine **2** could be initially formed and subsequently undergoes a ring–ring isomerization giving aziridinimine. We have also examined the basicity of both nitrogens in **1**. As expected, imino nitrogen, which is established as an electron-withdrawing group, exhibits a larger proton affinity. Overall, the ring moiety acts as the electron donor in which nitrogen favours the electron flow towards the exocyclic bond making

itself less suitable for an electrophilic attack. This results in a smaller proton affinity of the ring nitrogen in **1** than that of aziridine. The mobility of the ring nitrogen lone pair is also manifested in the ionized aziridinimine $\mathbf{1}Z^{+}$. While the radical is centred on the exocyclic N atom, π-donation takes place from the ring N to form an endocyclic C=N bond, thereby delocalizing the positive charge within the ring. We have also found an open distonic radical cation $\mathbf{1O}^{\bullet+}$ which is 128 kJ mol^{-1} more stable than $\mathbf{1}Z^{\bullet+}$. The transition structure for ring opening lies even lower than the vertically ionized aziridinimine. Thus both ions $\mathbf{1}Z^{\bullet+}$ and $\mathbf{1O}^{\bullet+}$ could be produced *e.g.* in a chemical ionization mass spectrometric experiment.

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