

# Amino, ammonio and aminioethenes: a theoretical study of their structure and energetics

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We have performed high level *ab initio* quantum mechanical calculations for aminoethene and the three isomeric 1,1- (*Z*)- or (*E*)-1,2-diaminoethenes as well as their singly and doubly charged cations derived by loss of electrons and/or upon protonation. Gas phase molecular structures were computed at the MP2/6-311 + G(3df,2p) level. Standard molar enthalpies of formation in the gas phase, at  $T = 298.15$  K, were estimated using the G3 composite method and atomization,isodesmic and homodesmotic reactions. Other energetic parameters were also calculated at the G3 level: proton affinities, basicities and adiabatic ionization enthalpies.

Theoretical and experimental data are compared. The reported experimental data refer only to aminoethene wherein the standard molar enthalpy of formation has a considerable uncertainty, although the molecular structure is well established. There are no such data, neither structural nor thermochemical, for any of the three isomeric diaminoethenes. Isoelectronic comparisons are made. For example, the diprotonated diaminoethenes are isoelectronic to isobutene and (*Z*)- and (*E*)-butene, while the doubly ionized diaminoethenes are likewise related to trimethylenemethane and 1,3-butadiene. Copyright © 2013 John Wiley & Sons, Ltd.

**Keywords:** aminoethenes; ammonioethenes; aminioethenes; enthalpy of formation; proton affinity; basicity; adiabatic ionization enthalpy

## INTRODUCTION

Enamines are an interesting and important class of organic compounds that have long been actively studied by synthetic, medicinally and mechanistically motivated chemists. Spectroscopists, calorimetrists and calculational chemists have also been so engaged,<sup>[1]</sup> although almost exclusively on substituted derivatives as opposed to the fundamentally and conceptually simpler and in principle, more informative parent species aminoethene (also called vinylamine and ethenamine). Interest in this species *per se* has long been frustrated because of its nonexistence: we are reminded of an over 70 year old study on the synthesis of its putative polymer almost plaintively thwarted by the nonexistence of the desired monomer.<sup>[2]</sup> Let us be more precise, the “transient polyatomic”<sup>[3]</sup> aminoethene and its related cations formed by protonation or electron loss have been observed in the gas phase where their synthesis has included pyrolysis/fragmentation of neutral or the corresponding species missing one electron, i.e. the radical cation, forms of acyclic amines (e.g. ref. 4), cyclic amines (e.g. cyclobutyl amine<sup>[5,6]</sup>), polycyclic amines (e.g. 11-amino-9,10-ethano-9,10-anthracene (e.g. ref. 7) and the reaction of ammonia with the singly ionized or radical cation forms of vinyl chloride and bromide.<sup>[8]</sup>

The molecular structure of the archetypal aminoethene was determined initially with microwave spectroscopy by Lovas *et al.*<sup>[9]</sup> The results from this study suggested that aminoethene has a non-planar structure due to a pyramidal amino group.<sup>[10]</sup> The structural nature of aminoethene is reproduced by diverse theoretical studies using partial retention of diatomic differential overlap (PRDDO), *ab initio* and density functional theory (DFT) calculations.<sup>[11–17]</sup>

Enediamines are also known but generally much more poorly understood than species with one amino group. For example, none of the three parent species, the three isomeric 1,1-; (*Z*)- or (*E*)-1,2-diaminoethenes, are known to the experimentalist; derived cations all but unknown.<sup>[18]</sup>

1,1-Diaminoethene is most commonly found as its tautomer acetamidine<sup>[19]</sup>, while the 1,2-diaminoethenes are not to be

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confused with the similarly sounding, but not even isomeric “ethylenediamine”. Compared to aminoethene, disappointingly few substituted derivatives of the diaminoethenes have been studied, e.g. ref. 20. The best known 1,2-diaminoethene derivatives are no doubt the related dyes indigotin (indigo) and its tetrabromo derivative tyrian purple. These species have been known for millennia and multiply reviewed in the chemical literature, e.g. references 21–23. However, these species are too functionalized to provide useful insights as paradigms for enediamine chemistry. A plausibly even older enediamine (in terms of synthesis) is diaminomaleonitrile, suggested as a key compound in the origin of life (e.g. ref 24). The mere presence of the two cyano groups hides its relation to simple enediamines. Thus, we turn to high level quantum chemical calculations to derive insights – in particular, we report below the results of our investigations on the three isomeric archetypal, unsubstituted 1,1-; (*Z*)- or (*E*)-1,2-diaminoethenes and for completeness corresponding calculations on aminoethene and the parent ethene itself with the expectation that knowledge of the parent species will provide guidance for the understanding of substituted species.

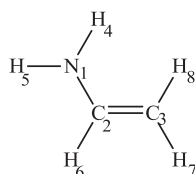
In this study, molecular structures were obtained at the MP2/6-311+G(3df,2p) level and standard molar enthalpies of formation in the gas phase, always at  $T=298.15\text{ K}$ , were estimated using the G3 composite method and atomization, isodesmic and homodesmotic reactions. Other energetic parameters were also calculated at the G3 level: proton affinities (*PA*), basicities and adiabatic ionizations enthalpies.

## COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian 03 program.<sup>[25]</sup>

In order to find the lowest energy conformer of aminoethene, we have calculated a potential energy surface (PES) at the MP2/6-311+G(3df,2p) level by varying the  $\text{H}_5\text{-N}_1\text{-C}_2\text{-C}_3$  dihedral angle ( $\phi$ ) from  $-180^\circ$  to  $180^\circ$  (see Fig. 1 for the atom numbering scheme on aminoethylene). This parameter includes both rotation around the C–N bond and nitrogen pyramidal inversion. In each point of the PES, the  $\text{H}_5\text{-N}_1\text{-C}_2\text{-C}_3$  dihedral angle was held fixed, while all the other geometric parameters were fully optimized. The dihedral angle was increased by a step of  $10^\circ$ .

We have also performed calculations to separate C–N rotation from N inversion in aminoethylene. We have scanned the  $\text{H}_5\text{-N}_1\text{-C}_2\text{-C}_3$  dihedral angle ( $\phi$ ) and also the  $\text{C}_2\text{-N}_1\text{-H}_4\text{-H}_5$  dihedral angle ( $\theta$ ). This second dihedral angle which corresponds to the nitrogen pyramidal inversion angle was centered at the nitrogen atom  $\text{N}_1$  and defined as the angle between the vector of the  $\text{C}_2\text{-N}_1$  bond and the plane defined by the three atoms,  $\text{N}_1$ ,  $\text{H}_4$  and  $\text{H}_5$ . We have scanned  $\phi$  from  $-180^\circ$  to  $180^\circ$  and  $\theta$  from  $-55^\circ$  to  $55^\circ$ , and the two were increased by a step of  $10^\circ$ . Each value of  $\theta$  corresponds to a different degree of nitrogen pyramidalization, where the positive values correspond to the amino hydrogen atoms pointing above the plane and the negative values below the plane:  $0^\circ$  corresponding to a planar geometry. In each point of the three-dimensional PES, the energy of the molecule is obtained



**Figure 1.** Atom numbering scheme for aminoethene

by fixing  $\phi$  and  $\theta$  and fully optimizing the remaining geometrical parameters at the MP2/6-311+G(3df,2p) level.

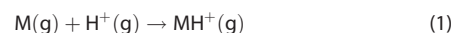
For the diaminoethenes, we have carefully checked different conformations in order to obtain the absolute minimum energy and not a relative, local minimum or saddle point conformer. The geometries of all aminoethenes were fully optimized at the MP2(full)/6-311+G(3df,2p) level and were further certified as true minima through construction and diagonalization of the corresponding Hessian matrix.

More reliable energy values were obtained using the G3<sup>[26]</sup> composite method. G3 is an improvement over G2<sup>[27]</sup> composite method and tries to reproduce effectively QCISD(T)/G3large energies through a series of calculations at lower level. The G3 large basis set is a slightly modified version of the 6-311+G(3df,2p) basis set used in the G2 procedure. The single-point energy calculations are performed on MP2(full)/6-31G(d) optimized geometries, and a higher level correction to compensate for remaining deficiencies is added as well as spin-orbit correction terms for the atoms.

The standard molar enthalpies of formation of the mono- and diaminoethenes were derived considering atomization and isodesmic and homodesmotic reactions.

G3 calculations were also extended to the mono- and diprotonated (addition of one and two protons) and mono- and dication (removal of one and two electrons) species. From these calculations, we were able to estimate gas phase *PA*, basicities and adiabatic ionization enthalpies of the aminoethenes.

The first gas phase *PA* and basicity of a molecule *M* are defined in terms of the hypothetical gas phase reaction:



The first gas phase *PA*(*M*,*T*) is the negative of the corresponding enthalpy change:

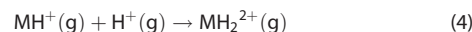
$$\text{PA}(\text{M}, T) = -\Delta H_r(T) \quad (2)$$

The first gas phase basicity of *M*, at temperature *T*, ( $\Delta G_{\text{basicity}}(\text{M}, T)$ ), is the negative of the Gibbs free energy change for this reaction

$$\Delta G_{\text{basicity}}(\text{M}, T) = -\Delta G_r(T) \quad (3)$$

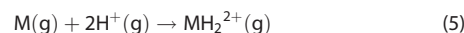
The difference between gas phase *PA* and basicity is that they refer, respectively, to enthalpy and free energy change.

The second gas phase *PA* and basicity of a molecule *M* is defined in terms of the hypothetical gas phase reaction:



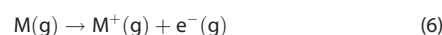
The second gas phase *PA* of *M*, at temperature *T*, is the negative of the corresponding enthalpy change, and the second gas phase basicity is the negative of the Gibbs free energy change.

The gas phase “first plus second (1+2)” *PA* ( $\text{PA}_{1+2}$ ) and basicity ( $\Delta G_{\text{basicity}1+2}$ ) of a molecule *M*, at temperature *T*, is defined in terms of the hypothetical gas phase reaction:



The gas phase  $\text{PA}_{1+2}$  is the negative of the corresponding enthalpy change, and the  $\Delta G_{\text{basicity}1+2}$  is the negative of the Gibbs free energy change.

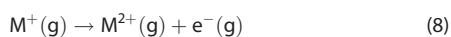
The first adiabatic ionization enthalpy (*IE*) of a molecule *M*, at temperature *T*, is defined in terms of the hypothetical gas phase reaction:



The first adiabatic *IE*, at temperature *T*, is the corresponding enthalpy change:

$$1^{\text{st}}\text{IE}(\text{M}, T) = \Delta H_r(T) \quad (7)$$

The second adiabatic ionization enthalpy of a molecule  $M$ , at temperature  $T$ , is defined in terms of the hypothetical gas phase reaction:



The second adiabatic ionization enthalpy ( $2^{nd} IE$ ), at temperature  $T$ , is the corresponding enthalpy change:

$$2^{nd} IE(M, T) = \Delta H_r(T) \quad (9)$$

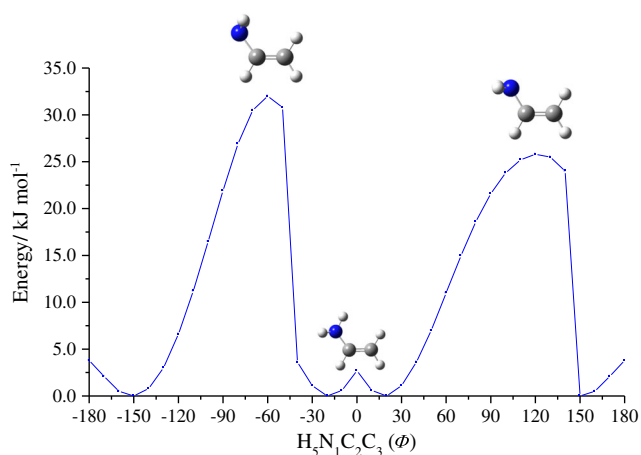
## RESULTS AND DISCUSSION

### Gas-phase molecular structures

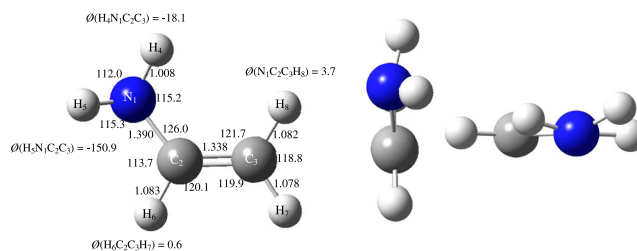
In our attempt to find the lowest energy conformer of aminoethene, we have varied the  $H_5-N_1-C_2-C_3$  dihedral angle ( $\Phi$ ) (see Fig. 1) to investigate the overall influence on the total energy of the molecule. This dihedral angle defines the orientation of the amino group relative to the carbon-carbon (CC) double bond. We have scanned  $\Phi$  from  $-180^\circ$  to  $180^\circ$ , increasing by a step of  $10^\circ$ . In each point of the PES, the energy of the molecule is obtained by fixing  $\Phi$  and fully optimizing the remaining geometrical parameters at the MP2/6-311 + G(3df,2p) level.

Figure 2 shows the computed PES: energy as function of the  $H_5-N_1-C_2-C_3$  ( $\Phi$ ) dihedral angle. As can be seen from this figure, the PES is approximately symmetrical around  $\Phi$ . It can also be observed that there is a significant energy barrier for rotation of  $\Phi$ . The conformations where  $\Phi$  is around  $-60^\circ$  and  $120^\circ$  have the highest energies. This can be attributed to the fact that stabilization by electronic delocalization between the lone pair on nitrogen and the CC double bond is at minimum. The conformation where the two hydrogen atoms from the amino group point towards the ethylene moiety ( $\Phi = -60^\circ$ ) has a higher energy than the one where the two hydrogen point away from the CC double bond ( $\Phi = 120^\circ$ ).

The four minima found consist of two symmetrically equivalent conformers:  $\Phi = -150^\circ / 150^\circ$  and  $\Phi = -20^\circ / 20^\circ$ . The most stable conformer was fully optimized at the MP2/6-311 + G(3df,2p) level of theory without any constraint. In Fig. 3, we show



**Figure 2.** Potential energy surface calculated at the MP2/6-311 + G(3df,2p) level for both rotation around the  $H_5-N_1-C_2-C_3$  dihedral angle and N pyramidal inversion in aminoethene



**Figure 3.** Front and side views of the most stable conformation of aminoethene obtained at the MP2/6-311 + G(3df,2p) level. Selected bond lengths are given in Å and angles in degrees

front and side views of the most stable conformation found for aminoethene. Selected bond lengths and bond angles were also included. As can be seen from Fig. 3, the aminoethene has a non-planar geometry (due to the fact that the nitrogen atom has a pyramidal geometry), in agreement with results from the microwave spectroscopy study by Lovas *et al.*<sup>[9]</sup> and previous computational studies.<sup>[11,13–16]</sup> In Table 1, we compare geometrical parameters obtained in this work with experimental data.<sup>[9]</sup> The calculated geometrical parameters are in very good agreement with the experimental data with deviations of less than 0.01 Å for the bond lengths and less than 3.1° for the bond angles. Some structural aspects of aminoethene are noteworthy. The geometry at the nitrogen is pyramidal, with angles slightly larger than tetrahedral. Pyramidalization at the nitrogen atom is coupled with torsion around the C–N bond so that the N–H bond *syn* to the CC double bond moves less out of the CCN plane than the other N–H bond. The vinyl group remains essen-

**Table 1.** Comparison between calculated (MP2/6-311 + G(3df,2p)) and experimental geometrical parameters for aminoethene<sup>a</sup>

Geometrical parameter	Aminoethene	
	Calc.	Exp. <sup>[9]</sup>
N <sub>1</sub> –C <sub>2</sub>	1.390	(1.397 ± 0.040)
C <sub>2</sub> –C <sub>3</sub>	1.338	1.335
N <sub>1</sub> –H <sub>4</sub>	1.008	1.010
N <sub>1</sub> –H <sub>5</sub>	1.007	1.010
C <sub>2</sub> –H <sub>6</sub>	1.083	1.09
C <sub>3</sub> –H <sub>7</sub>	1.078	1.09
C <sub>3</sub> –H <sub>8</sub>	1.082	1.09
N <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	126.0	(125.2 ± 2.0)
N <sub>1</sub> –C <sub>2</sub> –H <sub>6</sub>	113.7	–
H <sub>6</sub> –C <sub>2</sub> –C <sub>3</sub>	120.1	–
C <sub>2</sub> –C <sub>3</sub> –H <sub>8</sub>	121.7	123
C <sub>2</sub> –C <sub>3</sub> –H <sub>7</sub>	119.9	123
H <sub>7</sub> –C <sub>3</sub> –H <sub>8</sub>	118.8	118
H <sub>4</sub> –N <sub>1</sub> –C <sub>2</sub>	115.2	–
H <sub>5</sub> –N <sub>1</sub> –C <sub>2</sub>	115.3	–
H <sub>4</sub> –N <sub>1</sub> –H <sub>5</sub>	112.0	114
N <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub> –H <sub>6</sub>	3.7	–
H <sub>4</sub> –N <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	–18.1	–
H <sub>5</sub> –N <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	–150.9	–
H <sub>6</sub> –C <sub>2</sub> –C <sub>3</sub> –H <sub>7</sub>	0.6	–

<sup>a</sup>Bond lengths are in Å and angles in degrees.

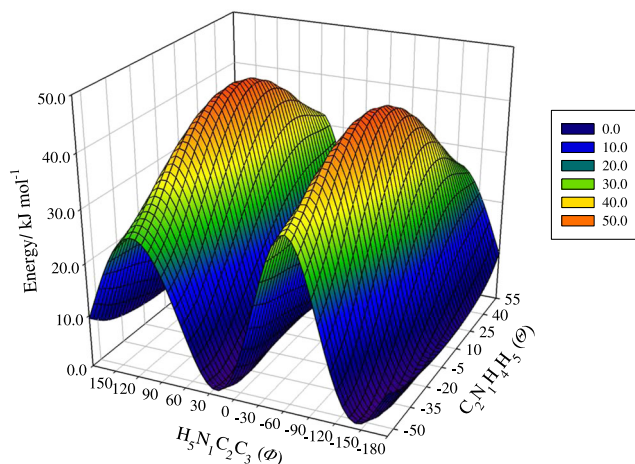
tially planar (dihedral angle  $H_6-C_2-C_3-H_7 = 0.6^\circ$ ).

The planar conformation of aminoethene was fully optimized at the MP2/6-311+G(3df,2p) level with only the constraint of a planar nitrogen configuration (the N–H bonds were frozen in the same plane as the vinyl group). The obtained planar structure was found to be  $3.7 \text{ kJ mol}^{-1}$  (MP2/6-311+G(3df,2p) energy difference) above the most stable conformation. This value is in encouragingly good agreement with the one obtained experimentally from Lovas *et al.*<sup>[9]</sup> microwave data for the barrier to N pyramidal inversion ( $4.5 \pm 0.3 \text{ kJ mol}^{-1}$  corroborating the quality of this calculation.<sup>[28]</sup>

The conformations  $\Phi = -60^\circ$  and  $\Phi = 120^\circ$  were also fully optimized at the MP2/6-311+G(3df,2p) level with only the constraint of a fixed dihedral angle  $\Phi$  and were found to be  $32.1 \text{ kJ mol}^{-1}$  and  $26.1 \text{ kJ mol}^{-1}$  (MP2/6-311+G(3df,2p) energy difference) above the most stable conformation. These barriers to rotation of the amino group are considerably higher than the barrier to N pyramidal inversion.

Rotation of  $\Phi$  angle leads not only to rotation around the C–N bond but also to pyramidal inversion at the nitrogen atom. That is why in Fig. 2, there are sudden drops in energy around the  $-45^\circ$  and  $145^\circ$  dihedral angles. Thus, we have performed calculations to separate C–N rotation from N pyramidal inversion. We have scanned the  $H_5-N_1-C_2-C_3$  ( $\Phi$ ) dihedral angle and also the nitrogen pyramidal inversion dihedral angle:  $C_2-N_1-H_4-H_5$  ( $\Theta$ ). Figure 4 shows the computed PES: energy as function of  $H_5-N_1-C_2-C_3$  ( $\Phi$ ) and  $C_2-N_1-H_4-H_5$  ( $\Theta$ ) dihedral angles. As can be seen from this figure, rotation around  $\Phi$  results now in smooth curves. The two energy barriers for C–N rotation increase as the hydrogen atoms from the amino group approach the plane of the molecule (as  $\Theta$  goes from  $55$  or  $-55^\circ$  to  $0^\circ$ ) and become equal when  $\Theta = 0^\circ$  (in this case, the PES is symmetrical around  $\Phi = -90^\circ$  and  $\Phi = 90^\circ$ ).

The geometries of the isomeric diaminoethenes were also fully optimized at the MP2/6-311+G(3df,2p) level of theory. In Fig. 5, we show front and side views of the most stable conformations found for the diaminoethenes. We observe that all diaminoethenes have non-planar geometries. In 1,1-diaminoethene and (Z)-1,2-diaminoethene, the two amino groups are oriented in opposite directions relative

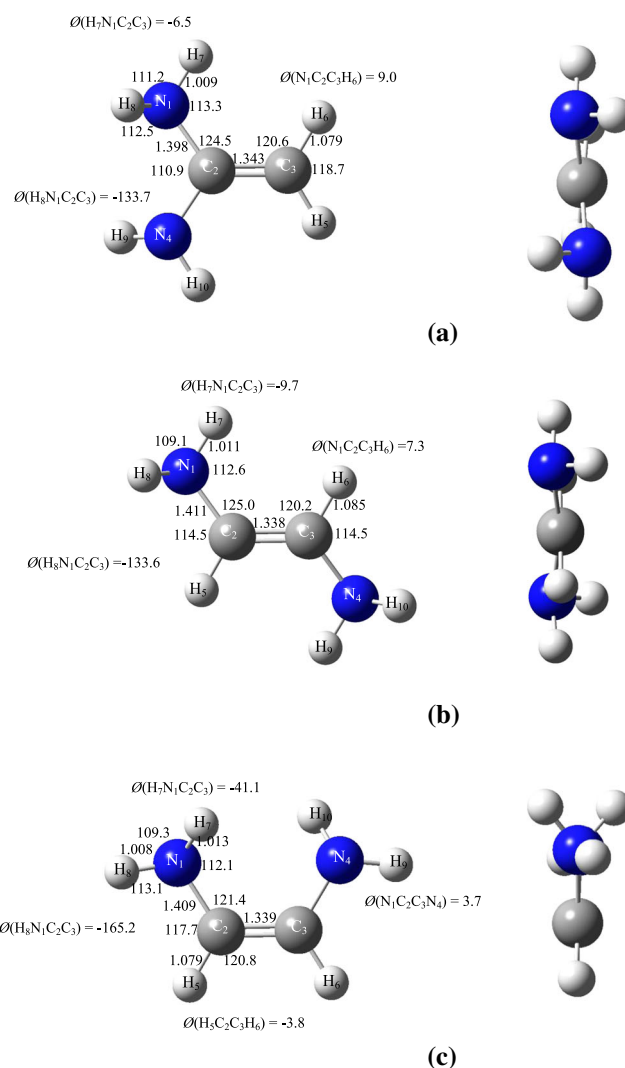


**Figure 4.** Potential energy surface of aminoethene calculated at the MP2/6-311+G(3df,2p) level as function of the  $H_5-N_1-C_2-C_3$  dihedral angle and the pyramidalization dihedral angle centred on the nitrogen atom  $C_2-N_1-H_4-H_5$

to ethylene moiety (the hydrogen atoms of both amino groups are two above and two below with respect to the ethylene moiety). On the other hand, in (E)-1,2-diaminoethene, the two amino groups are oriented in the same direction relative to ethylene moiety. We have not found in the literature experimental data regarding the molecular structures of the diaminoethenes with which we may compare our theoretical results.

### Enthalpies of formation

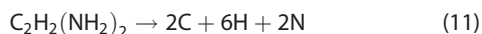
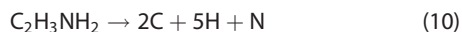
Experiment has not been particularly helpful in understanding the energetics of aminoethene and its derivatives. From gas phase ion energetics measurements and some assumptions about other poorly understood compounds, a value of  $(31 \pm 17) \text{ kJ mol}^{-1}$  was earlier suggested for the enthalpy of formation of aminoethene (refs 15,29,30). Should this value be trusted? There are few measured values for the enthalpy of formation of any enamine regardless of substitution<sup>[31]</sup> and the recommended uncertainty in the current value is uncomfortably large. This sug-



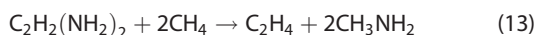
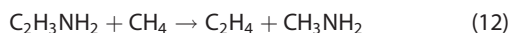
**Figure 5.** Front and side views of the MP2/6-311+G(3df,2p) optimized geometries of (a) 1,1-diaminoethene, (b) (E)-1,2-diaminoethene and (c) (Z)-1,2-diaminoethene. Selected bond lengths are given in Å and angles in degrees

gests we should be suspicious of this value. As such, the standard molar enthalpies of formation of the mono and diaminoethenes were derived using the following reactions:

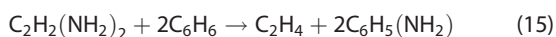
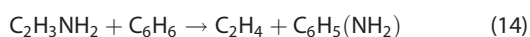
Set I:



Set II:



Set III:



The first set of equations represents the atomization reactions for aminoethene and for the three isomeric diaminoethenes. Atomization reactions are the standard procedure used in Gaussian-*n* theories to obtain enthalpies of formation. This procedure is particularly useful because the experimental values of the enthalpies of formation of the atoms are well known. The second and third sets of reactions are of the isodesmic type, that is, the number of bonds of each formal type is conserved on each side of the reactions. These reactions featuring a great similarity between reactants and products lead to the cancelation of errors inherent in quantum chemical calculations and thus, generally result in good estimates of enthalpies of formation. Furthermore, reactants and products of the reactions in the third equation set share an even larger similarity than in the second set as not only the number but also the type of bonds (hybridization of corresponding atoms) are conserved on both sides of the reactions, suggesting even greater reliability. Set III are recognized as homodesmotic reactions.

The enthalpies of formation for aminoethene and the diaminoethenes were obtained for each set of reactions. The enthalpies of formation were determined through the calculation of the enthalpy of the respective reactions in combination with the use of well-known values of enthalpies of formation for the auxiliary atoms or molecules. The calculated G3 absolute enthalpies, at  $T=298.15\text{ K}$ , for the aminoethenes and for all the auxiliary atoms and molecules used in this study as well as their experimental standard molar enthalpies of formation in the gas phase, at  $T=298.15\text{ K}$ , were collected in Table 2.

In Table 3, columns 2, 3 and 4, we show the G3 calculated reaction enthalpies of Sets I, II and III, at  $T=298.15\text{ K}$ , respectively, and in columns 4, 5 and 6, we show the derived standard molar enthalpies of formation for the aminoethenes, at  $T=298.15\text{ K}$ , respectively, from Sets I, II and III reactions. In the last column, we present experimental data only available for ethene and aminoethene. The only diaminoethene with a measured enthalpy of formation is indigotin,<sup>[34]</sup> this measurement is well over 100 years old, and so there is an immediate concern in regards to sample purity and methodological protocol. There is also a temperature uncorrected enthalpy of sublimation of indigotin<sup>[35]</sup> that requires a temperature correction of some 298 K to get to the standard temperature of 298 K – how do we correct for this?

The G3 estimate for ethene obtained using the atomization reaction is in excellent agreement with the experimental value, as it falls within the experimental uncertainty. For aminoethene, the computational estimates are higher than the “experimental” tabulated value. The “experimental” enthalpy of formation for aminoethene ( $(31 \pm 17)\text{ kJ mol}^{-1}$ ) is in fact derived from an approximate enthalpy of formation for acetaldimine,  $\text{CH}_3\text{CH}=\text{NH}$ , ( $(8 \pm 17)\text{ kJ mol}^{-1}$ ) and a theoretical isomerization energy between  $\text{CH}_3\text{CH}=\text{NH}$  and aminoethene, and so the experimental enthalpy of formation has a considerable uncertainty (See refs. 15,29–31). Indeed, the paucity of reliable thermochemistry on imines<sup>[36–40]</sup> suggests that the enthalpies of formation of both classes of compounds, enamines and imines, need reevaluation in concert with each other. The G3 estimates for the enthalpy of formation of aminoethene (58.7, 52.8 and 58.5  $\text{kJ mol}^{-1}$ ) are in encouragingly very good agreement with an estimate performed by Smith and Radom<sup>[15]</sup> at the MP4/6-311+G\*\* level (55  $\text{kJ mol}^{-1}$ )

**Table 2.** Calculated G3 absolute enthalpies, Gibbs free energies (in Hartree,  $E_h$ )<sup>a</sup> and experimental standard molar enthalpies of formation in the gas phase, at  $T=298.15\text{ K}$ , ( $\text{kJ mol}^{-1}$ ) of the aminoethenes and auxiliary atoms and molecules used in this work

Atom/Molecule	$H_{\text{G3}}$	$G_{\text{G3}}$	$\Delta_f H_m^0(\text{g})$
Ethene	-78.503417	-78.528268	$(52.5 \pm 0.3)^{[32]}$
Aminoethene	-133.824649	-133.854245	–
1,1-Diaminoethene	-189.151144	-189.183510	–
( <i>E</i> )-1,2-Diaminoethene	-189.135585	-189.168850	–
( <i>Z</i> )-1,2-Diaminoethene	-189.139845	-189.172926	–
Carbon ( $\text{C}^3\text{P}$ )	-37.825356	–	$(716.67 \pm 0.46)^{[33]}$
Hydrogen ( $\text{H}^2\text{S}$ )	-0.498642	–	$(217.999 \pm 0.006)^{[33]}$
Nitrogen ( $\text{N}^4\text{S}$ )	-54.561982	–	$(472.68 \pm 0.10)^{[33]}$
Methane	-40.453810	–	$-(74.4 \pm 0.4)^{[32]}$
Methylamine	-95.755734	–	$-(23.4 \pm 1.0)^{[32]}$
Benzene	-232.046754	–	$(82.6 \pm 0.7)^{[32]}$
Aminobenzene (aniline)	-287.368546	–	$(87.1 \pm 1.1)^{[32]}$

<sup>a</sup>Atomic unit of energy.  $1 E_h = 2625.49964\text{ kJ mol}^{-1}$ .

**Table 3.** G3 estimates of reaction enthalpies,  $\Delta_r H^\circ$ , (Sets I, II and III) and standard molar enthalpies of formation,  $\Delta_f H^\circ$ , of ethene and aminoethenes in the gas phase, at  $T = 298.15$  K ( $\text{kJ mol}^{-1}$ )

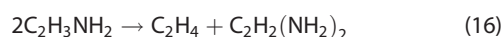
Molecule	$\Delta_r H^\circ$			$\Delta_f H^\circ$			Exp.
	G3			G3			
	Set I <sup>a</sup>	Set II <sup>b</sup>	Set III <sup>c</sup>	Set I <sup>a</sup>	Set II <sup>b</sup>	Set III <sup>c</sup>	
Ethene	2253.0	–	–	52.3	–	–	$(52.5 \pm 0.3)^{[32]}$
Aminoethene	2937.3	50.7	–1.5	58.7	52.8	58.5	$(31 \pm 17)^d$
1,1-Diaminoethene	3635.3	115.2	10.9	51.4	39.3	50.6	–
( <i>E</i> )-1,2-Diaminoethene	3594.5	74.4	–30.0	92.2	80.1	91.5	–
( <i>Z</i> )-1,2-Diaminoethene	3605.6	85.5	–18.8	81.0	69.0	80.3	–

<sup>a</sup>Reaction (10) was used for aminoethene and reaction (11) was used for the diaminoethenes.  
<sup>b</sup>Reaction (12) was used for aminoethene and reaction (13) was used for the diaminoethenes.  
<sup>c</sup>Reaction (14) was used for aminoethene and reaction (15) was used for the diaminoethenes.  
<sup>d</sup>See refs. [15,29–31].

using reaction (12), and so these values are trusted in the current study. The enthalpy of formation of aminoethene derived from reaction (12) is about  $5 \text{ kJ mol}^{-1}$  lower than the values derived from reactions (10) and (14) and the values for the diaminoethenes obtained from reaction (13) are about  $10 \text{ kJ mol}^{-1}$  lower than the ones derived from reactions (11) and (15). Recent quantum chemical calculations and accompanying analysis have suggested<sup>[41]</sup> that the enthalpy of formation of methylamine as determined experimentally is unreliable; discrepancies of a “few”  $\text{kJ mol}^{-1}$  were found for this species, the other methylamines and the methylated hydrazines.

1,1-Diaminoethene was found to be the most stable of the diaminoethenes and (*Z*)-1,2-diaminoethene more stable than (*E*)-1,2-diaminoethene. These relative stabilities follow from the *cis*- and *gauche* effects,<sup>[42–45]</sup> where there is generally greater stability of geminal over vicinal substituted ethenes and ethanes,<sup>[46–48]</sup> and the stabilizing effects of  $\gamma$ -aromaticity for  $6\pi$  “hetero” derivatives of olefins.<sup>[49,50]</sup> Notably, in a recent study by Santos and Ribeiro da Silva<sup>[51]</sup> on the energetics of diaminobenzenes, it was shown both experimentally and computationally that 1,2-diaminobenzene is more stable than the other two isomers. These authors suggest, based on experimental data, that this is due to the existence of intramolecular  $\text{N}\cdots\text{H}\cdots\text{N}$  hydrogen bonds. This hydrogen bonding is a plausibly stabilizing mechanism for 1,1- and (*Z*)-1,2-diaminoethene. In fact the  $\text{N}\cdots\text{H}$  distance in 1,2-diaminobenzene is  $2.457 \text{ \AA}$  and in 1,1- and (*Z*)-1,2-diaminoethene is  $2.472 \text{ \AA}$  and  $2.558 \text{ \AA}$ , respectively (values obtained from full geometry optimizations at the MP2/6-311 + G(3df,2p) level). These distances are smaller than the sum of the van der Waals radii of nitrogen and hydrogen (ca.  $2.6 \text{ \AA}$ ). This fact suggests that an intramolecular hydrogen bond is established although this interaction can be considered weak.

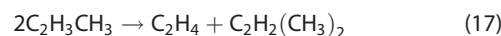
Another question relates to the effect that two amino groups have on the stability of the isomeric diaminoethenes. More precisely, it may be asked about the exothermicity or endothermicity of the reaction:



Let us use totally calculational data as found in Table 3 where we averaged the enthalpies of formation found from Eqns (10)/(11) (Set I) and (14)/(15) (Set III) for each species. So doing, 1,1-

diaminoethene is found to be stabilized by  $13.9 \text{ kJ mol}^{-1}$  relative to aminoethene while the (*E*)- and (*Z*)-1,2-diaminoethenes are destabilized by  $27.0$  and  $15.8 \text{ kJ mol}^{-1}$ , respectively. Entropy effects are plausibly small in reactions of gas phase species where the same number of molecules appears on the two sides. Taking the difference of  $H_{\text{G3}}$  and  $G_{\text{G3}}$  in Table 2, the discrepancies have the narrow range of  $3.3$  to  $5.2 \text{ kJ mol}^{-1}$  for  $\text{TS}_{\text{G3}}$ , the product of the entropy and (absolute) temperature. We will thus continue to give values for entropies but generally not discuss them and their consequence.

For comparison, we considered the methylated ethenes, i.e. propene and the isomeric butenes. While both stabilization and destabilization are exhibited for the related reactions



enthalpy changes are much smaller here than for the diamines. For the 1,1-, (*E*)- and (*Z*)-species, we find  $4.4 \text{ kJ mol}^{-1}$  stabilization,  $0.9 \text{ kJ mol}^{-1}$  stabilization and  $5.4 \text{ kJ mol}^{-1}$  destabilization, respectively, relative to propene using in this case, experimental data from Pedley's now “classic” database of the enthalpies of formation of organic compounds, ref. 32. That both stabilization and destabilization are seen shows that the *cis*-effect and geminal versus vicinal stabilization are not universal phenomena for the understanding of all disubstituted ethenes.

### Mono and diprotonated aminoethenes

G3 calculations have also been performed for the mono- and diprotonated aminoethene and diaminoethenes. In Table 4, we show the protonation site and the G3 calculated absolute enthalpies and Gibbs free energies, at  $T = 298.15$  K, for ethene and the monoprotonated aminoethenes. From these calculated results, we were able to calculate *PA* and basicities (alternatively written *GB* and  $\Delta G_{\text{basicity}}$ ) which are presented in Table 5. In this table, we also provide existing experimental values for comparison taken from the classic review of Hunter and Lias.<sup>[52]</sup> In the literature, there are experimental gas phase values of *PA* and  $\Delta G_{\text{basicity}}$  for only ethene and aminoethene.

Protonation of ethene does not give the ethyl cation as defined by C-protonation, i.e.  $\text{CH}_3\text{CH}_2^+$  is not formed. (As finally confirmed spectroscopically, this protonated cation is the non-classical hydrogen-bridged species.<sup>[53,54]</sup>) The G3 estimates of

**Table 4.** Protonation site and G3 calculated absolute enthalpies and Gibbs free energies (in Hartree,  $E_h$ )<sup>a</sup>, at  $T=298.15$  K, for the monoprotonated species studied in this work<sup>b,c</sup>

Monoprotonated species	Protonation site	$H_{G3}$	$G_{G3}$
Ethene	C	-78.759843	-78.787265
Aminoethene	C <sub>3</sub>	-134.174063	-134.204443
Aminoethene	N <sub>1</sub>	-134.150978	-134.181307
1,1-Diaminoethene	C <sub>3</sub>	-189.536904	-189.571013
1,1-Diaminoethene	N <sub>1</sub> = N <sub>4</sub>	-189.479054	-189.512974
(E)-1,2-Diaminoethene	C <sub>2</sub> = C <sub>3</sub>	-189.480200	-189.514463
(E)-1,2-Diaminoethene	N <sub>1</sub> = N <sub>4</sub>	-189.482388	-189.517078
(Z)-1,2-Diaminoethene	C <sub>2</sub> = C <sub>3</sub>	-189.495365	-189.528482
(Z)-1,2-Diaminoethene	N <sub>1</sub> = N <sub>4</sub>	-189.480989	-189.515676

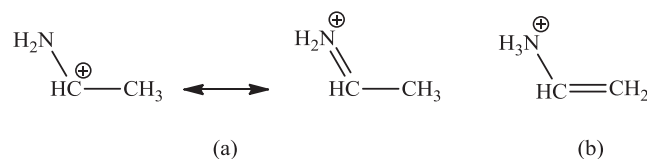
<sup>a</sup>Atomic unit of energy,  $1 E_h = 2625.49964 \text{ kJ mol}^{-1}$ .<sup>b</sup> $H(H^+) = 0.002360$  Hartree;  $G(H^+) = -0.010013$  Hartree.<sup>c</sup>See Figs. 3 and 5 for the numbering of the atoms.

PA and basicity for ethene are in excellent agreement with the experimental values.

Aminoethene can protonate at any of three plausibly basic sites, the nitrogen or at either of the two carbon atoms. We can conclude from the results presented in Table 4 that the preferred protonation site of aminoethene is the C<sub>3</sub> or beta (β) carbon atom, well-precedented from the "all-carbon" case of alkylation of general enamines (as shown in numerous chapters in the books and many primary publications referenced in [1]). When we protonate the C<sub>2</sub> or α carbon atom of aminoethene (see Fig. 3 for the numbering of the atoms), the hydrogen atom moves from the C<sub>2</sub> to the C<sub>3</sub> carbon atom, and we obtain the protonated species CH<sub>3</sub>-CH=NH<sub>2</sub><sup>+</sup>, identical to when we directly protonate the C<sub>3</sub> carbon atom. In no case was <sup>+</sup>CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> seen nor its collapsed form, the cyclic species which is protonated aziridine.

The PA of aminoethene has been determined experimentally by Ellenberger *et al.* [29,30] from ion cyclotron resonance spectroscopy measurements. However, most of the information about the preferred protonation site is from computational studies. The calculations performed in the last century were done either at the PRDDO or at the *ab initio* levels [11,13,15,29,55] and results pointed to aminoethene being a carbon and not nitrogen base. More recently, higher level calculations have been done. Chan

*et al.* [56] performed *post-Hartree-Fock* calculations at the MP2/Aug-cc-pVTZ//MP2/6-31 + G(d,p) level to obtain the protonation energies of a set of basic substrates including aminoethene. The values obtained for aminoethene were: 941.7 kJ mol<sup>-1</sup> at the β carbon atom and 884.9 kJ mol<sup>-1</sup> at the nitrogen atom. The PA of aminoethene was calculated to be 911.8 kJ mol<sup>-1</sup>. The authors have suggested that the preference for carbon protonation arises from the stability gained from delocalization of the positive charge, i.e. the resultant cation has resonance stabilization from contributions from both immonium and aminocarbenium cations (see Fig. 6(a)). DFT calculations have been performed by Álvarez *et al.* [57] at the B3LYP/6-311 + G(3df,3pd)//MP2/6-31 + G(d,p) level to derive the gas phase basicity of aminoethene, and the following values were obtained: 885.3 kJ mol<sup>-1</sup> for protonation in the β carbon atom and 838.1 kJ mol<sup>-1</sup> for protonated

**Figure 6.** Protonation of aminoethene at (a) C<sub>3</sub>, where the positive charge is delocalized, and (b) at N<sub>1</sub> where the charge is localized at N<sub>1</sub>**Table 5.** Protonation site and G3 calculated gas phase proton affinities (PA) and basicities ( $\Delta G_{\text{basicity}}$ ), at  $T=298.15$  K, for ethene and the aminoethenes

Molecule	Protonation site <sup>a</sup>	PA/ kJ mol <sup>-1</sup>		$\Delta G_{\text{basicity}}$ / kJ mol <sup>-1</sup>	
		G3	Exp. <sup>[52]</sup>	G3	Exp. <sup>[52]</sup>
Ethene	C	679.4	680.5	653.7	651.5
Aminoethene	C <sub>3</sub>	923.6	898.9	893.2	866.5
	N <sub>1</sub>	863.0		832.4	
1,1-Diaminoethene	C <sub>3</sub>	1019.0	—	991.9	—
	N <sub>1</sub> = N <sub>4</sub>	867.1		838.7	
(E)-1,2-Diaminoethene	C <sub>2</sub> = C <sub>3</sub>	911.0	—	881.1	—
	N <sub>1</sub> = N <sub>4</sub>	916.7		888.0	
(Z)-1,2-Diaminoethene	C <sub>2</sub> = C <sub>3</sub>	939.6	—	907.2	—
	N <sub>1</sub> = N <sub>4</sub>	901.9		873.6	

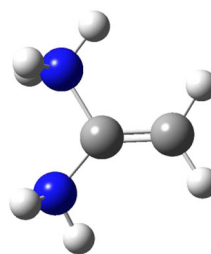
<sup>a</sup>See Figs. 3 and 5 for the numbering of the atoms.

ation in the nitrogen atom. These values are in good agreement with the ones obtained in this study. The authors have argued that the fact that the value of the gas phase basicity for the N-protonation was far away from the experimental value ( $866.5 \text{ kJ mol}^{-1}$ )<sup>[52]</sup> confirms that this compound is a carbon base and that protonation of the carbon atom is the preferred one in the gas phase. They deduced that the increase in the basicity relative to ethene was due to a resonance as opposed to inductive effect. Here, we note that carbon protonation is favored because of additional stabilization while protonation on nitrogen is disfavored because in the resulting cation, alternatively named ammonioethene and vinylammonium ion (see Fig. 6(b)), the vinyl group is electron withdrawing, which results in base weakening. In addition, the ammonio substituent on ethene as with strained rings has been shown to be destabilizing compared to the amino group.<sup>[12]</sup> A combined gas-phase ion molecule and calculational study<sup>[8]</sup> suggests the enthalpy of formation of vinylammonium ion is  $695 \text{ kJ mol}^{-1}$  or equivalently, C- ( $\beta$ ) PA is preferred by ca.  $38 \text{ kJ mol}^{-1}$  over that suggested therein for nitrogen protonation – this result is essentially unaffected upon use of the newest enthalpies of formation of the precursor vinyl chloride and bromide ions.<sup>[58]</sup>

Going from ethene to aminoethene, the PA and basicity markedly increase. As mentioned above, protonation on carbon is highly favored due to the delocalization of the positive charge as opposed to what happens in protonation on nitrogen. C-protonation is thus preferred over N-protonation even though we are much more used to amines than olefins as bases. G3 computed values of PA and basicity for C-protonation are closer than N-protonation to the experimental values by about  $10 \text{ kJ mol}^{-1}$ . We now note that amines prefer N-alkylation while enamines prefer C-alkylation, the latter being synthetically useful reactions of enamines and a primary interest in this class of compounds.<sup>[1]</sup>

Similar to aminoethene, the preferred protonation site of 1,1-diaminoethene is the  $C_3$  or  $\beta$ -carbon atom, and when we protonate the  $C_2$  or  $\alpha$  carbon atom (see Fig. 5), the hydrogen atom moves from the  $C_2$  to the  $C_3$  carbon atom, and we obtain the highly stable, protonated species acetamidinium ion  $\text{CH}_3\text{-C}(\text{NH}_2)=\text{NH}_2^+$  as when we protonate the  $C_3$  carbon atom. When we protonate a nitrogen atom ( $N_1$  or equivalently  $N_4$ ), we obtain the protonated species  $\text{CH}_2=\text{C}(\text{NH}_2)(\text{NH}_3)^+$  and in the most stable conformation of this species, there is no evidence for the existence of an intramolecular N–H...N hydrogen bond, see Fig. 7. The  $\text{CH}_2=\text{C}(\text{NH}_2)(\text{N})$  part of the molecule is nearly planar as is found in aminoethene itself. Attempts to calculate the conformation with one H atom directed to the amino group result in the  $\text{NH}_3^+$  group rotating and the final conformation is the one just discussed.

The preferred protonation site of (*E*)-1,2-diaminoethene is a nitrogen atom ( $N_1$  or equivalently  $N_4$ ) (see Fig. 5), and in the case of (*Z*)-1,2-diaminoethene the preferred protonation site is a carbon atom ( $C_2$  or equivalently  $C_3$ ). C-protonation ( $C_2$  or equivalently  $C_3$ ) of both (*E*)- and (*Z*)-1,2-diaminoethene gives origin to the protonated species  $\text{NH}_2\text{CH}_2\text{-CH}=\text{NH}_2^+$  (see Fig. 8). These two species are rotamers, and the one obtained from the (*Z*) isomer is more stable by  $34.1 \text{ kJ mol}^{-1}$  (G3 enthalpic difference) due to an intramolecular N–H...N hydrogen bond. The geometry of a transition state between the two species has been fully optimized at the MP2/6-311 + G(3df,2p) level, and the rotational barrier going from the (*Z*) to (*E*) rotamer was calculated to be of  $46.7 \text{ kJ mol}^{-1}$ , and the barrier going from rotamer (*E*) to (*Z*) was calculated to be  $10.3 \text{ kJ mol}^{-1}$ . In the case of N-protonation, we obtain the (*E*) and



**Figure 7.** MP2/6-311 + G(3df,2p) optimized structure of the N-monoprotonated 1,1-diaminoethene

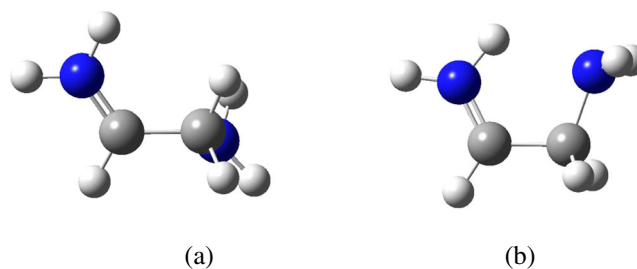
(*Z*) isomers of the species  $\text{NH}_2\text{CH}=\text{CHNH}_3^+$ . There is evidence for the existence of an intramolecular N–H...N hydrogen bond in the (*Z*) isomer, thereby sacrificing conjugation between the amino and ethene moieties, but even so the (*E*) isomer was found to be the most stable one by  $3.7 \text{ kJ mol}^{-1}$  (G3 enthalpic difference).

It should be noted that for C-protonation, the monoprotonated 1,1-diaminoethene is the most stable species, and the (*Z*)-1,2- is more stable than the (*E*)-1,2-diaminoethene.

Considering C-protonation, the marked increase in PA and basicity observed on going from ethene to aminoethene is not seen going from aminoethene to the diaminoethenes. There is a high increase in PA and basicity on going from aminoethene to 1,1-diaminoethene. By contrast, for (*Z*)-1,2-diaminoethene, there is only a small increase, and in the case of (*E*)-1,2-diaminoethene, there is even a decrease and N-protonation is preferred over C-protonation in this case.

It is interesting to note that the three monoprotonated diaminoethenes (at the nitrogen atom) are of comparable stability increasing in the order 1,1- < (*Z*)-1,2- < (*E*)-1,2-. This order is opposite to the free bases and is counter to any prediction based on stabilization dominated by the formation of N–H...N hydrogen bonds as well, i.e. (*E*)-1,2- < 1,1- < (*Z*)-1,2- (no hydrogen bonds < four-membered ring < five-membered ring). The significant difference of  $\text{NH}_2$  and  $\text{NH}_3^+$  groups has many precedents such as the ease and directionality of substitution of anilines and anilinium salts (*o*-/*p*- vs *m*-, respectively, from early in the undergraduate organic chemistry curriculum) and the qualitatively different singlet–triplet energy split of some substituted carbenes (singlet and triplet-stabilizing, respectively)<sup>[59,60]</sup>. Relatedly, we find that amides and their N-protonated derivatives are highly stabilized and significantly destabilized, respectively<sup>[61]</sup>.

In Table 6, we present, for the diprotonated aminoethenes, first and second protonation sites and the calculated G3 absolute enthalpies and Gibbs free energies, at  $T = 298.15 \text{ K}$ , and in Table 7, we explicitly give both atoms where proton-



**Figure 8.** MP2/6-311 + G(3df,2p) optimized structures of the  $C_3$  (or equivalently  $C_2$ ) protonated species in the case of (a) (*E*)-1,2-diaminoethene and (b) (*Z*)-1,2-diaminoethene



**Table 6.** First and second protonation sites and calculated G3 absolute enthalpies and Gibbs free energies (in Hartree,  $E_h$ )<sup>a</sup>, at  $T = 298.15$  K, of the diprotonated species

Diprotonated species	First protonation site	Second protonation site	$H_{G3}$	$G_{G3}$
Aminoethene	C <sub>3</sub>	N <sub>1</sub>	-134.922924	-134.954286
1,1-Diaminoethene	C <sub>3</sub>	N <sub>1</sub> (= N <sub>4</sub> )	-189.624573	-189.660097
1,1-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> )	N <sub>4</sub> (= N <sub>1</sub> )	-189.617902	-189.652006
(E)-1,2-Diaminoethene	C <sub>2</sub> (= C <sub>3</sub> )	N <sub>1</sub> (= N <sub>4</sub> )	-189.649142	-189.683589
(E)-1,2-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> )	N <sub>4</sub> (= N <sub>1</sub> )	-189.643303	-189.677643
(Z)-1,2-Diaminoethene	C <sub>2</sub> (= C <sub>3</sub> )	N <sub>1</sub> (= N <sub>4</sub> )	-189.642477	-189.676284
(Z)-1,2-Diaminoethene	C <sub>3</sub> (= C <sub>2</sub> )	N <sub>1</sub> (= N <sub>4</sub> )	-189.525019	-189.559366
(Z)-1,2-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> )	N <sub>4</sub> (= N <sub>1</sub> )	-189.626468	-189.661695

<sup>a</sup>Atomic unit of energy, 1  $E_h = 2625.49964$  kJ mol<sup>-1</sup>.**Table 7.** Protonation sites and G3 estimates of gas phase "first plus second" proton affinities ( $PA_{1+2}$ ) and basicities ( $\Delta G_{\text{basicity}_{1+2}}$ ), at  $T = 298.15$  K, for the aminoethenes

Molecule	Protonation sites <sup>a</sup>	$PA_{1+2}/$ kJ mol <sup>-1</sup>	$\Delta G_{\text{basicity}_{1+2}}/$ kJ mol <sup>-1</sup>
Aminoethene	C <sub>3</sub> + N <sub>1</sub>	2895.9	2835.6
1,1-Diaminoethene	C <sub>3</sub> + N <sub>1</sub> (= N <sub>4</sub> )	1255.4	1198.7
1,1-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> ) + N <sub>4</sub> (= N <sub>1</sub> )	1237.9	1177.5
(E)-1,2-Diaminoethene	C <sub>2</sub> (= C <sub>3</sub> ) + N <sub>1</sub> (= N <sub>4</sub> )	1360.7	1298.9
(E)-1,2-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> ) + N <sub>4</sub> (= N <sub>1</sub> )	1345.4	1283.3
(Z)-1,2-Diaminoethene	C <sub>2</sub> (= C <sub>3</sub> ) + N <sub>1</sub> (= N <sub>4</sub> )	1332.1	1269.0
(Z)-1,2-Diaminoethene	C <sub>2</sub> (= C <sub>3</sub> ) + N <sub>4</sub> (= N <sub>1</sub> )	1023.7	962.0
(Z)-1,2-Diaminoethene	N <sub>1</sub> (= N <sub>4</sub> ) + N <sub>4</sub> (= N <sub>1</sub> )	1290.0	1230.7

<sup>a</sup>See Figs. 3 and 5 for the numbering of the atoms.

ation occurs and G3 estimates of "gas phase first plus second (1 + 2)"  $PA$  ( $PA_{1+2}$ ) and basicities ( $\Delta G_{\text{basicity}_{1+2}}$ ), at  $T = 298.15$  K, for the aminoethenes.

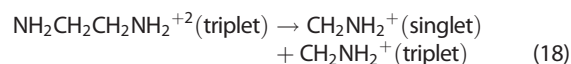
When we protonate aminoethene at both the C<sub>3</sub> and N<sub>1</sub> atoms, we obtain the diprotonated species  $\text{NH}_3\text{CHCH}_3^{2+}$ , assumed to be singlet by analogy to the stable isoelectronic  $(\text{CH}_3)_2\text{CH}^+$  carbocation.

Protonation at the C<sub>3</sub> and N<sub>1</sub> (or equivalently N<sub>4</sub>) atoms in 1,1-diaminoethene gives the diprotonated species  $\text{CH}_3\text{C}(=\text{NH}_2)\text{NH}_3^{2+}$  and protonation of both N atoms gives  $\text{H}_2\text{C}=\text{C}(\text{NH}_3)_2^{2+}$ . When we protonate both C atoms, one H atom from one of the carbon atoms moves to the nearest N atom and the final species is the same as if we had protonated the C<sub>3</sub> and N<sub>1</sub> atoms. When we protonate the C<sub>2</sub> and N<sub>1</sub> atoms, the H moves from the C<sub>2</sub> to the C<sub>3</sub> atom, and we also obtain the species as if we had protonated the C<sub>3</sub> and N<sub>1</sub> atoms.

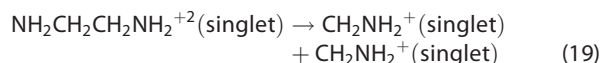
In (E)-1,2-diaminoethene, protonation at C<sub>2</sub> and N<sub>1</sub> gives the diprotonated species:  $\text{NH}_2\text{CHCH}_2\text{NH}_3^{2+}$ . When we protonate the C<sub>3</sub> and N<sub>1</sub> atoms, the H atom at the C<sub>3</sub> carbon atom moves to the C<sub>2</sub> carbon atom and we obtain the previous species. When we protonate both C atoms one of the H atoms moves to the adjacent amino group, and we obtain also the previous species. Protonation at both nitrogen atoms gives the diprotonated species  $\text{NH}_3\text{CH}=\text{CHNH}_3^{2+}$ .

In (Z)-1,2-diaminoethene, diprotonation at C<sub>2</sub> and N<sub>1</sub> gives the diprotonated species:  $\text{NH}_2\text{CHCH}_2\text{NH}_3^{2+}$ , protonation at C<sub>3</sub> and N<sub>1</sub> gives the diprotonated species:  $\text{NH}_2\text{CH}_2\text{CHNH}_3^{2+}$  and protonation at N<sub>1</sub> and N<sub>4</sub> nitrogen atoms gives the diprotonated species  $\text{NH}_3\text{CH}=\text{CHNH}_3^{2+}$ . When we protonate both C atoms, one of

the H atoms moves to the adjacent amino group, and we obtain the diprotonated species as if we had protonated C<sub>2</sub> and N<sub>1</sub>. If it were possible to force protonation of the two carbons, we would expect the resultant  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{2+}$  to fragment into two  $\text{CH}_2\text{NH}_2^+$  ions. The enthalpy of the following spin-allowed reaction:



at  $T = 298.15$  K, was calculated to be  $-300.7$  kJ mol<sup>-1</sup> at the MP2/6-311+G(3df,2p) level. The geometries of the three species were fully optimized at the MP2/6-311+G(3df,2p) level, and the obtained stationary points were characterized as minima through vibrational frequency calculations. The results suggest that  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{2+}$  (triplet) has a staggered conformation, the monocation  $\text{CH}_2\text{NH}_2^+$  singlet is planar and the CH<sub>2</sub> and the NH<sub>2</sub> of the monocation  $\text{CH}_2\text{NH}_2^+$  triplet are approximately in perpendicular planes. Assuming the same zero point energy, we have calculated the enthalpy of the following reaction:

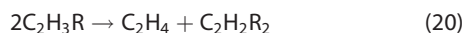


Starting with the aforementioned geometry of the triplet to calculate the singlet, during geometry optimization of the dication spontaneously splits in three fragments ( $\text{NH}_2 + \text{C}_2\text{H}_4 + \text{NH}_2$ ). Starting from the geometry of neutral

$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and calculating  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{+2}$  as singlet, the dication spontaneously splits in two ( $\text{CH}_2\text{NH}_2$ ).

Diprotonation of the  $\text{C}_2$  and  $\text{N}_1$  atoms in (*E*)- and (*Z*)-1,2-diaminoethene results in the protonated species  $\text{NH}_2\text{CHCH}_2\text{NH}_3^{+2}$  (see Fig. 9). These two species are rotamers, and the one obtained from the (*E*) isomer is more stable by  $17.5\text{ kJ mol}^{-1}$  ( $G_3$  enthalpic difference). The geometry of a transition state between the two species has been fully optimized at the MP2/6-311+G(3df,2p) level and the rotational barrier going from the rotamer was calculated to be of  $25.9\text{ kJ mol}^{-1}$  and the one going from the (*Z*) to the (*E*) rotamer was calculated to be  $8.2\text{ kJ mol}^{-1}$ .

A simple question relates to the enthalpy of formation of these doubly substituted species, the three isomeric diammonioethenes relative to the monosubstituted species. More precisely, we remember (cf. Eqn (17)) that within a  $10\text{ kJ mol}^{-1}$  range, regardless of the substitution pattern, the following reactions are thermoneutral for  $\text{R}=\text{CH}_3$

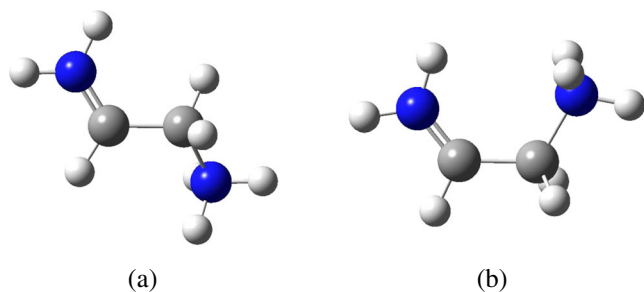


Not surprisingly because of the formation of a doubly charged cation, all three reactions for  $\text{R}=\text{NH}_2^+$  are significantly endothermic, 237, 204 and  $226\text{ kJ mol}^{-1}$  for the 1,1-, (*Z*)-1,2- and (*E*)-1,2-isomers. The order of increasing stability  $1,1- < (\text{Z})-1,2- < (\text{E})-1,2-$  is not surprising as it reflects the distance and hence repulsion of the two charged terminal atoms. What is surprising, perhaps, is how small the difference is for the reaction enthalpy of the three isomers.

Going from the mono- to the diaminoethenes, there is a high decrease in the  $\text{PA}_{1+2}$  and  $\Delta G_{\text{basicity}1+2}$  values. Considering the diaminoethenes, the *E* isomer has the highest values followed by the *Z* (except in the case of  $\text{C}_2 (= \text{C}_3) + \text{N}_4 (= \text{N}_1)$  diprotonation) and then the 1,1-.

### First and second adiabatic ionization enthalpies

We have also performed  $G_3$  calculations for the mono- and dications of the aminoethenes (species obtained by the loss of one and two electrons). In Table 8 and Table 9, we have collected the  $G_3$  absolute enthalpies and Gibbs free energy, at  $T=298.15\text{ K}$ , for the monocationic and the dicationic species, respectively. For the dications, calculations were performed considering that the dication is a singlet (multiplicity 1), or alternatively is a triplet (multiplicity 3). From these calculations, we were able to calculate first and second adiabatic ionization enthalpies ( $1^{\text{st}}IE$  and  $2^{\text{nd}}IE$ ), at  $T=298.15\text{ K}$ . In Table 10, we show the  $G_3$  calculated  $1^{\text{st}}IE$  and we find good agreement with the experimental values for ethene and aminoethene. We note that the



**Figure 9.** MP2/6-311+G(3df,2p) optimized structures of the  $\text{C}_2$  and  $\text{N}_1$  diprotated species in the case of (a) (*E*)-1,2-diaminoethene and (b) (*Z*)-1,2-diaminoethene

**Table 8.** Calculated  $G_3$  absolute enthalpies and Gibbs free energies (in Hartree,  $E_h$ )<sup>a</sup>, at  $T=298.15\text{ K}$ , for the monocationic species

Monocationic species	$H_{G_3}$	$G_{G_3}$
Ethene	-78.115047	-78.141107
Aminoethene	-133.525544	-133.555574
1,1-Diaminoethene	-188.880059	-188.913585
( <i>E</i> )-1,2-Diaminoethene	-188.886867	-188.920109
( <i>Z</i> )-1,2-Diaminoethene	-188.884024	188.917019

<sup>a</sup>Atomic unit of energy,  $1 E_h = 2625.49964\text{ kJ mol}^{-1}$ .

experimental *IE* values refer to the  $T=0\text{ K}$  and that calculated values in eV units at  $T=0\text{ K}$  are equal to the values at  $T=298.15\text{ K}$ . We have not found *IE* values for any of the three isomeric diaminoethenes in the experimental literature. On proceeding from ethene to aminoethene, the ionization enthalpy markedly decreases. In ionized ethene, there are two equivalent resonance structures  $\text{H}_2\text{C}^+-\text{CH}_2^+$  and  $\text{H}_2\text{C}^+-\text{CH}_2^+$ , and their equivalence results in stabilization. When one amino group is introduced, the two structures are no longer the same,  $\text{H}_2\text{C}^+-\text{CHNH}_2^+$  and  $\text{H}_2\text{C}^+-\text{CH}^+(\text{NH}_2)$ , and while there is less stabilization due to symmetry, the multi eV stabilization of alkyl cations by amino groups more than compensates for this loss (either ref. 62 and/or ref. 63–65); aminoethene is stabilized relative to ethene radical cation.

When there are two amino groups, whether situated 1,1-, (*Z*)-1,2- or (*E*)-1,2-, there is additional stabilization in the resulting isomeric diaminoethenes but two are not as good as one: diaminoethenes are not twice as stabilized as aminoethene.

In Table 11, we show the  $G_3$  calculated  $2^{\text{nd}}IE$ . The singlet dications of (*E*)- and (*Z*)-1,2-diaminoethene (1,2-diaminoethene,  $\text{N,N}'$ -diprotated 1,4-diaza-1,3-butadiene) are the same species. These ions are isoelectronic to 1,3-butadiene. As deduced spectroscopically, butadiene has two rotamers, the *trans* and the *gauche*.<sup>[66–70]</sup> The latter would be destabilized for the current doubly charged ion because of electrostatic repulsion between the terminal atoms. This unique rotamer of the singlet dication of 1,2-diaminoethene is the (*E*)- or *trans*-oid. It is not surprising that the singlet dication of 1,1-diaminoethene is less stable than that of the 1,2-isomer. First, the nitrogens are closer to each other in the 1,1-isomer increasing electrostatic repulsion. Second, to the extent that the 1,2-dication isoelectronically relates to 1,3-butadiene, the dication of the 1,1-diamino species might be assumed to mimic methylenecyclopropane, (**1**) (see Fig. 10 for structural formula of numbered species). With methylenecyclopropane having a “super-strained” three-membered ring (i.e. significantly more than that of the significantly strained cyclopropane itself<sup>[71–73]</sup>) and an enthalpy of formation ca.  $90\text{ kJ mol}^{-1}$  higher than that of 1,3-butadiene,<sup>[32]</sup> the resulting ring-closed diazoniacyclopentane (**2**) would be even more relatively destabilized because of charge repulsion between adjacent positive nitrogens. Accepting these isoelectronic analogies, we should not be surprised that the singlet dication of 1,1-diaminoethene is considerably higher in energy than that of its 1,2-isomer.

On the other hand, for the triplet, simple Hückel MO logic suggests a higher  $\text{C}_2-\text{C}_3$  bond order than in 1,3-butadiene (**3**) itself, and so, both (*Z*)- and (*E*)-1,2-diaminoethene dication (**4**) and (**5**), respectively) are sensibly separate energy minima. Charge

**Table 9.** Calculated G3 absolute enthalpies and Gibbs free energies (in Hartree,  $E_h$ )<sup>a</sup>, at  $T=298.15$  K, for the dicationic species

Dicationic species	(1) $H_{G3}^b$	(1) $G_{G3}^b$	(3) $H_{G3}^c$	(3) $G_{G3}^c$
Ethene	-77.463511	-77.488823	-77.235753	-77.263010
Aminoethene	-132.933774	-132.963792	-132.857141	-132.888301
1,1-Diaminoethene	-188.323856	-188.358172	-188.297535	-188.330347
( <i>E</i> )-1,2-Diaminoethene	-188.413946	-188.446749	-188.288396	-188.324281
( <i>Z</i> )-1,2-Diaminoethene	-188.413952	-188.446746	-188.278321	-188.312644

<sup>a</sup>Atomic unit of energy, 1  $E_h = 2625.49964$  kJ mol<sup>-1</sup>.  
<sup>b</sup>Multiplicity of the singlet dication = 1.  
<sup>c</sup>Multiplicity of the triplet dication = 3.

repulsion reasoning correctly suggests the latter to be more stable. We would not have thought that whatever provides the stabilizing mechanism for general 1,1-disubstituted species relative to their 1,2-isomers would be "enough" to result in the triplet 1,1-diaminoethene dication still being ca. 90 kJ mol<sup>-1</sup> more stable than that of its 1,2-isomer. Singlet 1,1-diaminoethene dication, CH<sub>2</sub>=C(NH<sub>2</sub><sup>+</sup>)<sub>2</sub> (**6**) is calculated to be ca. 70 kJ mol<sup>-1</sup> more stable than its triplet counterpart, while the formally isoelectronic trimethylenemethane<sup>[74,75]</sup> CH<sub>2</sub>=C(CH<sub>2</sub>)<sub>2</sub> (**7**) is more stable than its singlet by about the same amount. This difference may be understood in terms of simple resonance structure logic. Trimethylenemethane may be described as ethene doubly substituted in its 1-position by -CH<sub>2</sub> groups. Alternatively, it may be described as an allyl radical substituted by in the 1-position by -CH<sub>2</sub> group, (**8**). Either description suggests non-interacting radical sites and so by Hund's rule, a triplet ground state is suggested. On the other hand, singlet 1,1-diaminoethene dication is plausibly described by a formamidinium cation HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> wherein the hydrogen on carbon is replaced by a -CH<sub>2</sub><sup>+</sup> group, i.e. <sup>+</sup>CH<sub>2</sub>-C(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> (**9**). As both fragments have no unpaired electrons, the current cation is sensibly a ground state singlet wherein the CH<sub>2</sub>-C(N)<sub>2</sub> dihedral angle singlet in the 1,1-diaminoethene dication is 180.0°, i.e. the molecule is completely planar. Both the 1,2-isomers of trimethylenemethane and 1,1-diaminoethene dication are sensibly singlet as both ·CH<sub>2</sub>-CH=CH-CH<sub>2</sub>· and <sup>+</sup>NH<sub>2</sub>-CH=CH-NH<sub>2</sub><sup>+</sup> can readily "move electrons" by "arrow pushing" to form the ground state singlet species CH<sub>2</sub>=CH-CH=CH<sub>2</sub> and <sup>+</sup>NH<sub>2</sub>=CH-CH=NH<sub>2</sub><sup>+</sup>. For the former, a recent experiment shows that<sup>[76]</sup> the singlet is more stable by 248.5 kJ mol<sup>-1</sup>. For the latter, the singlet is more stable by 329.6 kJ mol<sup>-1</sup>. This is consistent with experience: butadiene,

however reactive, is most assuredly a closed-shell species. And certainly, in that aminium ions are less stable than immonium ions then, the bis-aminium ion <sup>+</sup>NH<sub>2</sub>-CH=CH-NH<sub>2</sub><sup>+</sup> will be significantly less stable than the bis-immonium ion, <sup>+</sup>NH<sub>2</sub>=CH-CH=NH<sub>2</sub><sup>+</sup>.

**Table 11.** G3 calculated second adiabatic ionization enthalpies (2<sup>nd</sup> $I/E$ ), at  $T=298.15$  K, for ethene and the aminoethenes<sup>a</sup>

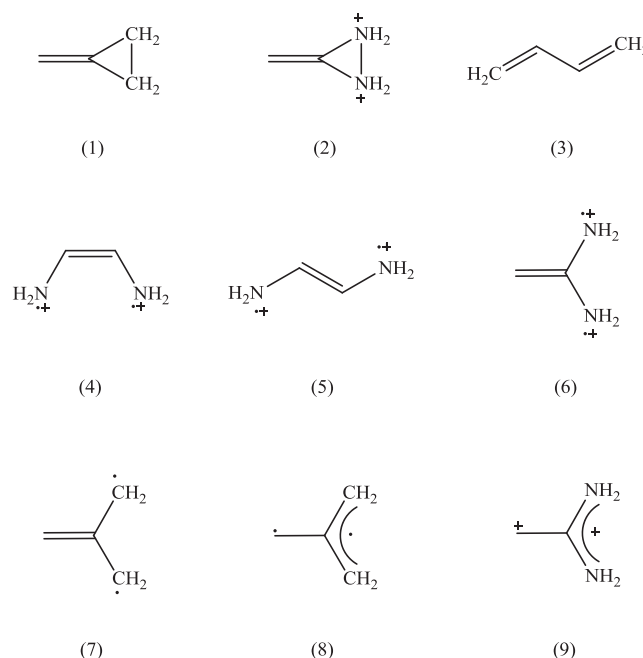
Molecule	(1)2 <sup>nd</sup> $I/E/$ eV <sup>b</sup>	(3)2 <sup>nd</sup> $I/E/$ eV <sup>c</sup>
Ethene	17.7	23.9
Aminoethene	16.1	18.2
1,1-Diaminoethene	15.1	15.9
( <i>E</i> )-1,2-Diaminoethene	12.9	16.3
( <i>Z</i> )-1,2-Diaminoethene	12.8	16.5

<sup>a</sup>1 Hartree = 27.2114 eV; 1 eV = 96.4853 kJ mol<sup>-1</sup>.  
<sup>b</sup>Considering the multiplicity of the dication = 1.  
<sup>c</sup>Considering the multiplicity of the dication = 3.

**Table 10.** G3 calculated first adiabatic ionization enthalpies (1<sup>st</sup> $I/E$ ), at  $T=298.15$  K, for ethene and the aminoethenes<sup>a</sup>

Molecule	1 <sup>st</sup> $I/E/$ eV	
	G3	Exp.
Ethene	10.6	(10.5138 ± 0.0006) <sup>[62]</sup>
Aminoethene	8.1	8.6 <sup>[4]</sup>
1,1-Diaminoethene	7.4	—
( <i>E</i> )-1,2-Diaminoethene	6.8	—
( <i>Z</i> )-1,2-Diaminoethene	7.0	—

<sup>a</sup>1 Hartree = 27.2114 eV; 1 eV = 96.4853 kJ mol<sup>-1</sup>.

**Figure 10.** Structural formula of studied species

## CONCLUSIONS

The present theoretical study allowed us to obtain new and important structural and energetic parameters that characterize the gas phase chemistry of amino, ammonio and aminoethenes. The most stable conformations of aminoethene and the three isomeric diaminoethenes were computed with MP2/6-311+G(3df,2p) level of theory. Although the gas phase molecular structure of aminoethene is well known and agrees closely with computational results, those calculated for the three isomeric diaminoethenes are first reported in this study. Computed G3 standard enthalpies of formation, *PA*, basicities and adiabatic ionization enthalpies were compared with experimental data available only for the case of aminoethene. Good agreement between theory and experiment was found except for the standard molar enthalpy of formation for aminoethene. Computational calculations suggest a value about 25 kJ mol<sup>-1</sup> higher than the literature "experimental" value (31 ± 17) kJ mol<sup>-1</sup>. 1,1-Diaminoethene was found to be the most stable of the diaminoethenes and (Z)-1,2-diaminoethene more stable than (E)-1,2-diaminoethene. For the singly charged radical ion, the stability is in the reverse order: (E)-1,2- > (Z)-1,2- > 1,1-. The computation of gas phase *PA* and basicities confirms previous experimental and computational studies that aminoethene prefers to protonate the carbon rather than the nitrogen atom. The preferred protonation site of 1,1- and (Z)-1,2-diaminoethene was found to be a carbon atom, while in the case of (E)-1,2-diaminoethene, the preferred protonation site is a nitrogen atom. For C-protonation, the increasing order of stability of the monoprotonated diaminoethenes was found to be: (E)-1,2 < (Z)-1,2 < 1,1-, and for N-protonation, the increasing order of stability was: 1,1- < (Z)-1,2- < (E)-1,2-. Of the diverse diprotonated diamines wherein the nitrogens and/or carbons were protonated, (E)-1,2-diaminoethene was found to be the most stable, plausibly explained by minimizing charge repulsion. The doubly ionized diaminoethenes, were studied as both singlets and triplets, and the singlet (E)-1,2-species, recognizable as isoelectronic to 1,3-butadiene, was found to be the most stable isomer.

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