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Gaseous protonated nitrosamide. A G2 theoretical study on the structure, stability, and interconversion of $(H_2N\text{-}NO)H^+$ isomers [1]

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Abstract

The $(H_2N\text{–}NO)H^+$ potential energy surface has been investigated at the G2 level of theory. The ion–dipole adduct $H_3N\text{–}NO^+$ **1** is the most stable protomer, and the proton affinity of $H_2N\text{–}NO$ is computed as 191.3 kcal mol^{-1}. The $H_2N\text{–}N\text{–}OH^+$ ion **2** and $H_2N\text{–}NH\text{–}O^+$ ion **3** are less stable than **1** by 2 and 13 kcal mol^{-1}, respectively. All the isomers lie into deep potential wells, and should be in principle observed as distinguishable species in the gas phase. Our theoretical data are used to discuss the conceivable structure of the gaseous protonated nitrosamide recently observed by Egsgaard et al.

1. Introduction

The role of X–NO (X = H, NH_2, OH, and F) in combustion [1–3], atmospheric [4–7], and interstellar chemistry [8] stimulates great interest in their detailed structure, bonding, and properties [9–14]. As a part of our interest in gaseous protonated inorganic molecules [15], we have recently employed mass spectrometric techniques and high-level of theory ab initio calculations to investigate the structure, stability, and interconversion of gaseous $(X\text{–}NO)H^+$ isomers (X = H [16,17], OH [18], OMe [19], and F [20]). We became therefore interested in the structure and stability of the gaseous protonated nitrosamide, $(H_2N\text{–}NO)H^+$, recently observed by Egsgaard et al. from the ionization of NH_3/NO mixtures in a chemical ionization source [21]. They assume the exclusive formation of $H_3N\text{–}NO^+$ as the primary product and rule out its conceivable isomerization to $H_2N\text{–}N\text{–}OH^+$ by computing, at the semiempirical level of theory, an interconversion barrier of ca. 86 kcal mol^{-1}. A subsequent independent ab initio [22] study was exclusively focused on structural and thermochemical aspects of $H_3N\text{–}NO^+$ and $H_2N\text{–}N\text{–}OH^+$ and does not provide the details which are required for a proper discussion of gas-phase experiments involving $(H_2N\text{–}NO)H^+$. The present G2 calculations, aimed at obtaining an accurate description of the $(H_2N\text{–}NO)H^+$ potential energy surface, suggest that the $H_3N\text{–}NO^+$ assignment of the observed $H_3N_2O^+$ ions should be reconsidered and that additional and more refined experiments are required to

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[1] Dedicated to Professor Fulvio Cacace on the occasion of his 65th birthday.

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safely assign the structure of gaseous protonated nitrosamide.

2. Computational details

The ab initio calculations have been performed using a RISC/6000 version of the Gaussian 94 set of programs [23]. The geometries of the investigated species were optimized at the HF/6-31G* and MP2/6-31G* level of theory (the latter was used without frozen core orbitals and will be denoted as MP2(FULL)/6-31G*) and their harmonic vibrational frequencies were computed at both computational levels. Approximate QCISD(T)/6-311 + G(3df,2p) energies were calculated at the MP2(FULL)/6-31G* optimized geometries using the Gaussian-2(G2) procedure [24] implemented as a standard routine in Gaussian 94. This computational method is amply recognized as able to reproduce or predict unknown thermochemical data (atomization energies, ionization potentials, electron affinities, and

Table 1
List of the MP2(FULL)/6-31G* optimized parameters of H_2N–NO and the $(H_2N\text{–}NO)H^+$ isomers 1–3 (for the labeling of the atoms, see Fig. 1)

Species	Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
H_2N–NO (C_1)	N1–N2	1.341	N1–N2–O	113.0	H1–N1–N2–O	10.5
	N2–O	1.236	H1–N1–N2	117.9	H2–N1–N2–O	167.8
	N1–H1	1.019	H2–N1–N2	115.9		
	N1–H2	1.010				
1a (C_s)	N1–N2	2.056	N1–N2–O	112.3	H2–N1–N2–O	121.6
	N2–O	1.128	H1–N1–N2	114.2		
	N1–H1	1.025	H2–N1–N2	107.0		
	N1–H2	1.024				
1b (C_s)	N1–N2	2.060	N1–N2–O	112.2	H3–N1–N2–O	61.4
	N2–O	1.128	H1–N1–N2	105.1		
	N1–H1	1.023	H2–N1–N2	111.6		
	N1–H2	1.024				
2a (C_s)	N1–N2	1.260	N1–N2–O	110.3		
	N2–O	1.308	H1–N1–N2	122.0		
	N1–H1	1.032	H2–N1–N2	115.7		
	N1–H2	1.024	H3–O–N2	105.8		
	O–H3	0.989				
2b (C_s)	N1–N2	1.265	N1–N2–O	118.0		
	N2–O	1.291	H1–N1–N2	125.5		
	N1–H1	1.032	H2–N1–N2	114.6		
	N1–H2	1.026	H3–O–N2	115.2		
	O–H3	0.997				
2c (C_1)	N1–N2	1.253	N1–N2–O	112.0	H1–N1–N2–O	1.3
	N2–O	1.350	H1–N1–N2	122.6	H2–N1–N2–O	183.7
	N1–H1	1.036	H2–N1–N2	115.9	H3–O–N2–N1	283.2
	N1–H2	1.030	H3–O–N2	110.9		
	O–H3	0.989				
3 (C_s)	N1–N2	1.296	N1–N2–O	124.4		
	N2–O	1.222	H1–N1–N2	117.1		
	N1–H1	1.026	H2–N1–N2	119.5		
	N1–H2	1.022	H3–N2–N1	116.0		
	N2–H3	1.042				

proton affinities) of compounds containing first- and second-row atoms with a target accuracy of ±2 kcal mol^{-1}. Within the G2 theory, the zero-point vibrational energies (ZPEs) are derived from the HF/6-31G* frequencies scaled by 0.8929. The obtained 0 K total energies, G2(0 K), are corrected at 298.15 K, G2(298.15 K), by adding the translational (3/2 *RT*), rotational (*RT* or 3/2 *RT* for linear and non-linear species, respectively), and vibrational contributions at this temperature. The last term is calculated by standard statistical mechanics [25] formulas using the scaled HF/6-31G* vibrational frequencies. As a final, the 298.15 K energy differences are corrected to enthalpy differences by assuming ideal gas behaviour and adding the proper ΔnRT contribution.

3. Results and discussion

3.1. Structure and stability of H_2N–NO

The elusive nitrosamide has been recently demonstrated to be stable in the dilute gas phase [26]. We have preliminarily optimized its geometry at the MP2(FULL)/6-31G* level of theory and computed its G2 total energy. Our obtained structure, depicted in Fig. 1 and detailed in Table 1, is fully consistent with previously discussed MP2/6-31G** data [12]. In particular, H_2N–NO is predicted to be non-planar (C_1 symmetry) with an out-of-plane deviation of the NH_2 group of ca. 10°. Using the G2(298.15 K) energies of H, N, and O, obtainable from the literature [24] and H_2N–NO, reported in Table 3, the 298.15 K atomization enthalpy of the molecule is evaluated as 371.1 kcal mol^{-1}. Combining this value with the experimental [27] enthalpies of formation of H, 52.1 kcal mol^{-1}, N, 113.0 kcal mol^{-1}, and O, 59.6 kcal mol^{-1}, the experimentally unreported enthalpy of formation of H_2N–NO is theoretically evaluated as 18.7 kcal mol^{-1}.

3.2. Structure and stability of the $(H_2N\text{–}NO)H^+$ isomers

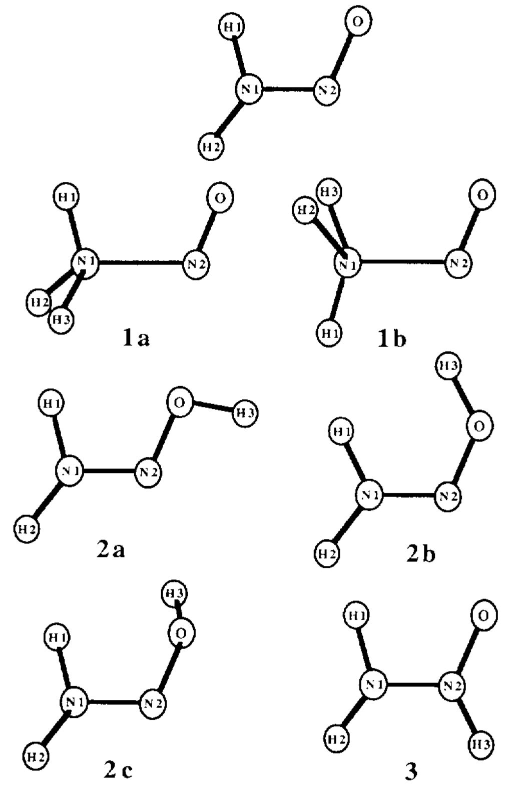

Fig. 1. Connectivities of H_2N–NO and the $(H_2N\text{–}NO)H^+$ ions **1**–**3**.

Fig. 1 shows the connectivity of the $H_3N\text{–}NO^+$, $H_2N\text{–}N\text{–}OH^+$, and $H_2N\text{–}NH\text{–}O^+$ ions **1a**–**b**, **2a**–**c**, and **3** located as stationary points on the MP2(FULL)/6-31G* potential energy surface. Their detailed geometries and relevant energy data are reported in Tables 1 and 3, respectively.

We found two distinct conformers of $H_3N\text{–}NO^+$, but only **1a** revealed a true energy minimum. Consistent with our previous findings on the structure of gaseous $HX\text{–}NO^+$ (X = OH [18], OMe [19], and F [20]), and in line with the results of recent MP2/6-31G(d,p) calculations [22], this isomer is characterized as an ion–dipole complex between NO^+ and NH_3. The N1–N2 distance, 1.341 Å in H_2N–NO, is as long as 2.056 Å, and the N2–O distance, 1.128 Å, is only slightly longer than free NO^+, 1.103 Å. Ion **1b** is structurally similar to **1a** but possesses one imaginary frequency of 48.7i cm^{-1}. It is the conformational transition structure for the rotation of the NH_3 group of ion **1a** around the N1–N2 bond. From Table 3, this motion is practically barrier-free. In fact, at 0 K, ion **1b** is less stable than **1a** by less than 0.1 kcal mol^{-1} and becomes more stable than **1a** by

0.5 kcal mol^{-1} if one includes the 298.15 K corrections (we note that we are excluding the contribution from the imaginary vibrational frequency to the thermal energy of **1b**).

Both the *trans* conformer **2a** and the *cis* conformer **2b** of $H_2N-N-OH^+$ revealed true energy minima. From Fig. 1 and Table 1, attachment of the proton to the oxygen atom of H_2N-NO results in an appreciable elongation of the N2–O bond, which passes from 1.236 Å in H_2N-NO to 1.308 Å in ion **2a** and 1.291 Å in ion **2b**. In addition, increasing of the positive charge on the N2–O group enhances back donation from N1 by an extent which is similar in the two ions. In fact, the N1–N2 distance of H_2N-NO, 1.341 Å, decreases to 1.260 and 1.265 Å in **2a** and **2b**, respectively. Thus, the significant energy difference computed between the two isomers, 10.9 kcal mol^{-1} at the G2(298.15 K) level of theory, likely reflects the unfavourable eclipsing of H1 and H3 in the *cis* conformer **2b**. In fact, from Table 1, we note that all the bond angles other than H2–N1–N2 are flatter in **2b** rather than in **2a**. For example, the N1–N2–O angles are computed as 110.3° (ion **2a**) and 118.0° (ion **2b**). The interconversion of **2a** and **2b** occurs through the conformational transition structure **2c**. The computed imaginary frequency, 762.3i cm^{-1}, refers to the out-of-plane rotation of H3, which lies almost perpendicular to the plane defined by the NH_2 and NO moieties. From Table 3, the energy demanding for this interconversion is computed as 19.4 kcal mol^{-1} with respect to **2a**.

The $H_2N-NH-O^+$ ion **3** has been as well characterized as a true energy minimum. From Fig. 1 and Table 1, attachment of a proton to N2 enhances back donation from N1. Thus, if compared with H_2N-NO, ion **3** is fully planar, and, for example, the N1–N2 distance reduces from 1.341 to 1.296 Å.

The relative stability of the $(H_2N-NO)H^+$ protomers **1a**, **2a**, and **3** deserves careful discussion. From Table 3, ion **1a** is undoubtedly more stable than **3**. In fact, their G2(298.15 K) energy difference amounts to 13.9 kcal mol^{-1}. However, the difference between **1a** and **2a** is as low as 2 kcal mol^{-1}. If one takes into account the accepted accuracy of the G2 calculations, this finding suggests caution in predicting the most basic site of H_2N-NO on purely thermochemical grounds. However, consistent with the character of loosely bound species of ion **1a**, if one includes the entropy contribution to the relative stability of isomers **1a** and **2a**, calculated using the scaled HF/6-31G* frequencies, at 298.15 K the free energy of **1a** is computed to be lower than **2a** by ca. 5 kcal mol^{-1}. This suggests *the NH_2 group of H_2N-NO as the thermodynamically favoured protonation site.*

3.3. The proton affinity of H_2N-NO and the NO^+ affinity of NH_3

Assuming the formation of H_3N-NO^+ and using the G2(298.15 K) energies of H_2N-NO and **1a** reported in Table 3 we calculate the proton affinity (PA) of H_2N-NO, i.e. the minus enthalpy change of the reaction

$$H_2N-NO + H^+ \rightarrow H_3N-NO^+$$

as 191.3 kcal mol^{-1}. Combining this value with our derived theoretical enthalpy of formation of H_2N-NO and the experimental enthalpy of formation of H^+, 365.7 kcal mol^{-1}, one obtains a theoretical enthalpy of formation of H_3N-NO^+ of 193.1 kcal mol^{-1}. Using this value and the experimental enthalpies of formation of NH_3, −11.0 kcal mol^{-1}, and NO^+, 235.3 kcal mol^{-1}, the NO^+ affinity (NOA) of NH_3, i.e. the enthalpy change of the reaction

$$H_3N-NO^+ \rightarrow NH_3 + NO^+$$

is evaluated as 30.7 kcal mol^{-1}. This is practically coincident with the purely theoretical estimate of 31.1 kcal mol^{-1} obtained from the G2 (298.15 K) total energies of H_3N-NO^+, NH_3 and NO^+ reported in Table 3 and provides reassuring evidence for the internal consistency of our G2 calculations. We note here that our recently reported [20] NOAs of H_2O, 18.5 kcal mol^{-1}, and MeOH, 25.3 kcal mol^{-1}, follow the expected trend, i.e. NOA (H_2O) < NOA (MeOH) < NOA (NH_3). In addition, including the NOAs of HF and MeF, presently evaluated as 12.7 and 16.8 kcal mol^{-1}, respectively [2] one obtains

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[2] The G2(298.15 K) total energies (atomic units) are as follows: $HF-NO^+$: −229.76349; $MeF-NO^+$: −268.97360; HF: −100.34765; MeF: −139.55129.

the following correlation between the PAs of these simple ligands and their NOAs:

$$\mathrm{NOA(kcal\,mol^{-1})} = -13.29 + 0.213\,\mathrm{PA(kcal\,mol^{-1})}.$$

The dependence is reasonably linear (correlation coefficient = 0.978) despite the large covered range of PAs ((PA(HF) = 117.0 kcal mol^{-1}, PA(NH_3) = 204.0 kcal mol^{-1}) and the difference in the nature of the atoms involved in the ligation with NO^+.

3.4. Interconversion of the $(H_2N\text{–}NO)H^+$ isomers

The small enthalpy differences between the $(H_2N\text{–}NO)H^+$ isomers indicate that they can be successfully observed, at least in principle, as distinguishable isomers in the gas phase only if residing into potential wells separated by significant energy barriers. We have therefore located their connecting transition structures on the MP2(FULL)/6-31G* potential energy surface. The connectivity of the obtained ions **4**, **5**, and **6** is shown in Fig. 2, and their detailed geometries and relevant energy data are collected in Tables 2 and 3, respectively. In addition, Fig. 3 schematizes the relative stability of all the presently investigated $(H_2N\text{–}NO)H^+$ ions.

The four-centers transition structure **4** connects ions **1a** and **2b**. The imaginary frequency, 1452.1i cm^{-1}, refers to the in-plane motion of the hydrogen H1 migrating from N1 to O. The N1–H1 distance, 1.536 Å, is remarkably longer than $H_3N\text{–}NO^+$, 1.025 Å, and, overall, a significant structural rearrangement is required to overcome the activation barrier.

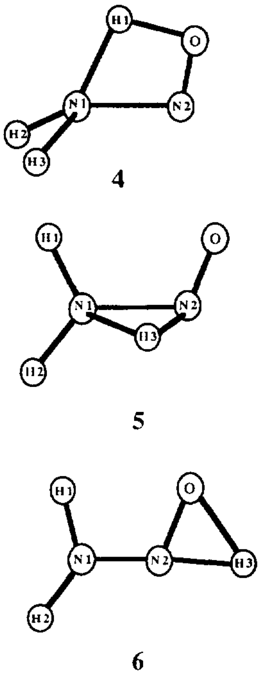

Fig. 2. Connectivities of the $(H_2N\text{–}NO)H^+$ ions **4**–**6**.

Table 2
List of the MP2(FULL)/6-31G* optimized parameters of the 4–6 $(H_2N\text{–}NO)H^+$ ions 4–6 (for the labeling of the atoms, see Fig. 2)

Species	Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
4 (C_s)	N1–N2	1.441	N1–N2–O	100.6	H2–N1–N2–O	238.3
	N2–O	1.236	H1–N1–N2	71.3		
	N1–H1	1.536	H2–N1–N2	108.9		
	N1–H2	1.035	H1–O–N2	91.0		
	O–H1	1.201				
5 (C_1)	N1–N2	1.455	N1–N2–O	118.7	H1–N1–N2–O	359.4
	N2–O	1.199	H1–N1–N2	120.2	H2–N1–N2–O	147.8
	N1–H1	1.039	H2–N1–N2	113.1	H3–N1–N2–O	233.4
	N1–H2	1.034	H3–N1–N2	52.2		
	N1–H3	1.406				
	N2–H3	1.260				
6 (C_s)	N1–N2	1.282	N1–N2–O	121.2		
	N2–O	1.289	H1–N1–N2	118.3		
	N1–H1	1.031	H2–N1–N2	117.8		
	N1–H2	1.023	H3–N2–O	64.3		
	N2–H3	1.189	H3–O–N2	54.2		
	O–H3	1.321				

Consistently, from Table 3, at the G2 (298.15 K) level of theory the energy demanding for this isomerization is computed as high as 57.7 kcal mol^{-1}. The three centers transition structure **5** connects isomers **1a** and **3**. The single imaginary frequency of 2034.6i cm^{-1} refers to the motion of H3 from N1 to N2, and the significant differences in the geometries of **1a** and **5** (e.g. N1–N2 shortens from 2.056 to 1.455 Å and N1–H3 increases from 1.024 to 1.406 Å) are in line with the high activation barrier, computed as 75.1 kcal mol^{-1} at the G2 (298.15 K) level of theory. As a final, we have located ion **6** as the transition structure for the interconversion of **2a** into **3**. This is also a high energy path, which requires to overcome an activation barrier of 60.7 kcal mol^{-1}. The single imaginary frequency of **6**, 2100.7i cm^{-1}, refers to the in-plane motion of H3 which migrates from N2 to O.

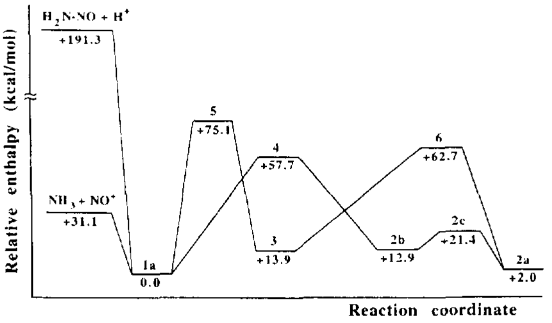

Fig. 3. G2(298.15 K) relative enthalpies of the $(H_2N{-}NO)H^+$ ions.

3.5. Implications for gas-phase experiments on $(H_2N{-}NO)H^+$

Based on the potential energy diagram depicted in Fig. 3 we feel appropriate to make here certain considerations on the detailed structure of the gaseous protonated nitrosamide recently obtained from the ionization of NH_3/NO mixtures [21]. If one assumes the direct association (likely barrier free) of NH_3 and NO^+ as the only ion–molecule reaction leading to $H_3N_2O^+$, the $H_3N{-}NO^+$ assignment by Egsgaard et al. appears plausible. In fact, from Fig. 3, the exothermicity of this association, 31.1 kcal mol^{-1}, is well below the energy barrier for the isomerization of **1a** into any alternative $(H_2N{-}NO)H^+$ isomer. However, as already pointed out by Egsgaard et al., formation of $H_3N{-}NO^+$ could as well occur by direct association of $NH_3^{·+}$ and $NO^·$. Using our theoretical enthalpy of formation of **1a**, 193.1 kcal mol^{-1}, and the experimental enthalpies of formation of $NH_3^{·+}$, 223.2 kcal mol^{-1}, and $NO^·$, 21.8 kcal mol^{-1}, the exothermicity of this process is evaluated as ca. 52 kcal mol^{-1}. This is indeed a lower limit if one considers the conceivable excitation of $NH_3^{·+}$ from the ionization event. Therefore, one can not safely rule out that the energy gained in the association of $NH_3^{·+}$ and $NO^·$ becomes comparable, or even

Table 3
Zero-point energies and total energies (atomic units) and relative energies (kcal mol^{-1}) of all the investigated molecules and ions

Species (NIMAG [a])	ZPE [b]	G2 (0 K)	G2 (298.15 K)	Δ*E* (298.15 K)
H_2N-NO (0)	0.03222	−185.60203	−185.59849	
1a (0)	0.04222	−185.90597	−185.90092	0.0
1b (1)	0.04215	−185.90586	−185.90168	−0.5
2a (0)	0.04598	−185.90100	−185.89767	+2.0
2b (0)	0.04550	−185.88365	−185.88029	+12.9
2c (1)	0.04391	−185.86996	−185.86678	+21.4
3 (0)	0.04569	−185.88230	−185.87878	+13.9
4 (1)	0.03979	−185.81237	−185.80902	+57.7
5 (1)	0.03878	−185.78462	−185.78117	+75.1
6 (1)	0.03839	−185.80488	−185.80107	+62.7
NO^+ (0)	0.00580	−129.39888	−129.39652	
				+30.5
NH_3 (0)	0.03304	−56.45864	−56.45578	

[a] Number of imaginary frequencies.
[b] Scaled HF/6-31G*.

larger, than the activation barriers for the isomerization of **1a** into **2b** or **3**, presently computed as ca. 58 and 75 kcal mol^{-1}, respectively. As a result, one should obtain ions of $H_2N-N-OH^+$ and/or $H_2N-NH-O^+$ connectivity. In addition, one can not exclude the possible occurrence, in the chemical ionization source, of complex reaction sequences which lead to the direct formation of $H_2N-N-OH^+$ and/or $H_2N-NH-O^+$. From Fig. 3, both of these isomers are trapped into potential wells deep enough to prevent their facile dissociation and/or isomerization.

In our opinion, the above considerations suggest caution in the detailed structural assignment of the $H_3N_2O^+$ ions obtained from the ionization of NH_3/NO. This process could lead to isomers other than H_3N-NO^+ or more likely, to mixtures of isomeric structures. Structurally-diagnostic techniques, such as collisionally activated dissociation spectrometry, are in principle expected to provide useful indication. In addition, our theoretical results suggest that independent structural information could be also obtained by investigating the thermochemistry and the reactivity of the $H_3N_2O^+$ ions. For example, both H_3N-NO^+ and $H_2N-N-OH^+$ should undergo proton transfer to bases whose PA is larger than ca. 190 kcal mol^{-1}, but only the ion–dipole adduct H_3N-NO^+ should undergo facile NO^+ transfer to ligands whose NOA is larger than 31 kcal mol^{-1}.

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