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Protonation Thermochemistry of α,ω-Alkyldiamines in the Gas Phase: A Theoretical Study

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The proton affinities (PA) of the three first members of the series of α,ω-alkyldiamines, 1,2-ethanediamine (**1**), 1,3-propanediamine (**2**), and 1,4-butanediamine (**3**), were calculated at the G2(MP2) level. [PA(M) = 947.7, 977.7, and 999.8 kJ/mol for M = **1, 2, 3**, respectively.] Protonation entropies, $\Delta S°_p = S°(MH^+) - S°(M)$, were estimated by explicitly considering the rotational barriers of the torsional modes in both the neutral molecules M = **1, 2, 3** and their protonated forms MH^+. Calculated protonation entropy values are −17, −29, and −46 $J \cdot mol^{-1} \cdot K^{-1}$ for **1, 2, 3,** respectively. Combining the calculated PA and $\Delta S°_p$ lead to calculated gas-phase basicities [$GB_{calc}(M)$ = 910.3, 936.9, and 953.6 kJ/mol for **1, 2, 3**, respectively] in excellent agreement with experiment. [$GB_{exp}(M)$ = 912.4, 940.0, and 954.4 kJ/mol for **1, 2, 3**, respectively.]

1. Introduction

Influence of both functional groups on the acid−base properties of aliphatic bifunctional species is a subject of fundamental interest in organic chemistry. From this point of view, α,ω-alkyldiamines are compounds of choice because they can develop internal hydrogen bonding in their neutral and in their protonated forms. Gas-phase protonation energetics of the first members of the series of α,ω-alkyldiamines was studied experimentally more than 20 years ago by ion cyclotron resonance[1] and pulsed electron beam, high-pressure mass spectrometry.[2,3] A clear enhancement of the gas-phase basicities of these molecules with respect to primary amines of comparable polarizability was observed. This has been explained by the formation of a strong internal hydrogen bond in the protonated forms of the diamines, a proposal which has been corroborated by the observation of an entropy loss upon protonation.[2,3] However, if, after correction to the reevaluated basicity scale,[4] the gas-phase basicities determined in ref 1−3 agree nicely, this is not the case for the entropic terms quoted in ref 2 and 3. This leads to large uncertainties on the proton affinity values of these compounds. It is now well established that high-level molecular orbital calculations provide accurate proton affinities in addition to valuable information on the structures and conformations of the parent molecules and their protonated forms. In this study, we examine theoretically the three first members of the series, α,ω-alkyldiamines: 1,2-ethanediamine (**1**), 1,3-propanediamine (**2**), and 1,4-butanediamine (**3**). Calculations of their proton affinities has been done at the G2(MP2) level and estimates of their protonation entropies by means of ab initio molecular orbital methods taking into account the rotational barriers of the torsional modes.

2. Computational Section

Standard ab initio calculations have been performed using the Gaussian-94 series of programs.[5] Standard G2(MP2) theory[6] uses a geometry optimized at the MP2(full)/6-31G(d) level and a scaled (by a factor 0.893) HF/6-31G(d) zero-point energy (ZPE). A base energy calculated at the MP2/6-311G(d,p) level is corrected by several additivity approximations to QCISD(T) and to the 6-311+G(3df,2p) basis set. To account for residual basis set deficiencies, G2(MP2) theory introduces higher-level corrections (HLC) that depend on the number of paired and unpaired electrons. G2(MP2) formalism yields, in general, reliable heats of formation, ionization energies, and proton affinities. At this level of theory, the accuracy of these calculated enthalpic quantities is better than 5 kJ/mol, as established recently for a set of ca. 150 compounds.[7]

Heats of formation have been evaluated from the G2(MP2) total energies by considering the atomization reactions.[8] Using this approach, the heat of formation at 0 K for a given species *X*, $\Delta_f H°_0(X)$, is given by:

$$\Delta_f H°_0(X) = \Sigma\Delta_f H°_0(\text{atoms}) - \Sigma E[\text{G2(MP2)}](\text{atoms}) + E[\text{G2(MP2)}](X) \quad (1)$$

The heat of formation at 298 K is therefore given by:

$$\Delta_f H°_{298}(X) = \Delta_f H°_0(X) + \Delta_{298}H°(X) - \Sigma\Delta_{298}H°(\text{elements}) \quad (2)$$

where the difference between the enthalpy at 298 K and 0 K is represented by the terms $\Delta_{298}H°$ ($\Delta_{298}H° = H°_{298} - H°_0$). For the elements, experimental $\Delta_{298}H°$ values have been used (i.e., 8.468, 1.050, and 8.669 kJ/mol for $H_{2(g)}$, $C_{(s)}$, and $N_{2(g)}$ respectively), whereas, for the other species, the translational and rotational contributions were taken equal to 3 RT and the vibrational contribution estimated from the scaled (by a factor 0.8929) HF/6-31G(d) vibrational frequencies.

The calculation of absolute third law entropies uses standard statistical thermodynamic formulas through a procedure similar to the E2 method described by Radom et al.[9] Each vibrational contribution to entropy was computed according to the standard equation:

$$S° = R\,[(\theta/T)/(e^{\theta/T} - 1) - \ln(1 - e^{-\theta/T})] \quad (3)$$

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where $\theta = h\nu/k_B$, where h and k_B are the Planck 's and Boltzman's constants, respectively, and using the scaled harmonic vibrational frequencies ν calculated at the HF/6-31G(d) level. Entropies for internal rotations were computed by using the hindered rotor model developed by Pitzer.[10] In this approach, the energy levels of a rotor associated with a potential energy barrier of the form $V_0/2\ (1 - \cos n\phi)$, where ϕ is the dihedral angle, are found with the help of a one-dimensional Schrödinger equation. The results are presented as a function of two dimensionless variables: V_0/RT and $1/Q_{fr}$ (i.e., the reciprocal of the partition function for the free rotation). In practice the entropy of a given rotor is obtained by addition of a corrective term to the entropy calculated under the free rotor approximation, $S°_{fr}$:

$$S°_{fr} = 1/2R \ln[8\pi^3 e I_{red} k_B T/n^2 h^2] \tag{4}$$

where $e = 2.71828$ and I_{red} the reduced moment of inertia of the two rotating groups around the axis containing the twisting bond.

In this study, the required rotational potential energy barriers, V_0, were obtained at the HF/6-31G(d) level using a relaxed rotation approach (i.e., all geometrical parameters were optimized except the dihedral angle considered). The possibility of hysteretic loops and catastrophes in the potential energy vs dihedral angle curves had been emphasized during this type of exploration.[9b] However, such situations are generally detected by abrupt energy changes, and this has been carefully checked in the present study. For the purpose of comparison, the harmonic vibrational frequencies of the torsional modes were also calculated using the relationship:

$$\nu = (n/2\pi)(V_0/I_{red})^{1/2} \tag{5}$$

The rotation of asymmetric rotors generates nonequivalent conformations corresponding to various minima of the potential energy curve $V_0(\phi)$. The total entropy of such a mixture of conformers may be determined according to eq 6, where x_i represents the molar fractions of conformer i:

$$S° = \Sigma x_i S°_i - R\Sigma x_i \ln x_i \tag{6}$$

If the energy differences between conformers are small, the entropy of mixing, $R\Sigma x_i \ln x_i$, may be approximated by $R \ln n_c$, where n_c is the total number of conformers. Thus the correction for mixing exactly compensates for the degeneracy of the rotors, which is accounted for by the factor n in eqs 4 or 5. The $S°_i$ terms should be similar for the conformers considered, because the internal rotations do not produce considerable changes in the principal moments of inertia or in the vibrational frequencies. We thus consider that the term $\Sigma x_i S°_i$ may be equated with the $S°$ of the most stable conformation.

The detailed geometries and vibrational frequencies used in the present work are available upon request from the authors.

3. Results and Discussion

As recalled in the Introduction, the gas-phase protonation energetics of α,ω-alkyldiamines **1**−**4** had been determined experimentally some years ago.[1−3] Each kind of experiment involves the determination of the equilibrium constant of a proton-transfer reaction between the studied diamine and a reference base. The experimental data, after anchoring to the reevaluated basicity scale,[4] lead to the gas-phase basicities of **1**−**4** reported in Table 1. It is immediately apparent that the deduced gas-phase basicity (GB) values agree nicely from one laboratory to one another; a standard deviation of less than ±2 kJ/mol is generally observed for a given compound. The corresponding averaged GB values were selected in the compilation by Hunter and Lias[4]; these numbers are also recalled in Table 1. What is less firmly established is the entropic term $\Delta S°_p = S°(MH^+) - S°(M)$ for which a considerable spread (30 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) is observed between the experimental results of ref 2 and 3, although similar techniques had been used. Considering the relationship $PA(M) = GB(M) + T\ [\Delta S°_p - S°_{H^+}]$ this large discrepancy leads also to considerable uncertainty about the proton affinity value PA(M); differences as large as 12 kJ/mol are observed in Table 1. Note that the PA(M) values tabulated in ref 4 are not averaged values but estimates based on the averaged GB(M) and a selected $\Delta S°_p$ term.

TABLE 1: Summary of Experimental Thermochemical Data Concerning the Protonation of Diamines 1−4

M	GB(M) (kJ/mol)	$\Delta S°_p$ ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)	PA(M) (kJ/mol)	ref
1, 1,2-ethanediamine	915.6	−51[a]	963.2	1
	910.9	−55.1[b]	959.7	2
	912.0	−22.1 ± 3.3[b]	951.0	3
	912.5 ± 2.1	−22.1	951.6	4
2, 1,3-propanediamine	942.4	−61[a]	993.1	1a
	939.6	−61[a]	990.3	1b
	938.7	−80.6[b]	995.1	2
	939.7	−48.6 ± 1.4[b]	986.6	3
	940.0 ± 1.6	−49	987	4
3, 1,4-butanediamine	955.1	−97[a]	1016.4	1a
	954.3	−97[a]	1015.6	1b
	953.7	−61.7[b]	1004.5	3
	954.3 ± 0.7	−63	1005.6	4
4, 1,5-pentanediamine	947.9	−109[a]	1012.8	1a
	944.4	−109[a]	1009.3	1b
	945.0	−78.1[b]	1000.7	2
	946.2 ± 1.8	−70	999.6	4

[a] Estimated by considering the entropy of the corresponding *n*- and cyclo-alcanes. [b] From a Van t'Hoff plot of high-pressure mass spectrometric data.

In this study, the structural and energetic changes occurring during the protonation of molecules **1**−**3** has been investigated theoretically. The entropy differences $\Delta S°_p$ were estimated using a method taking into account the hindrance of internal rotations, as described in the computational section. Proton affinities and heats of formations have been calculated at the G2(MP2) level. Combining these two kinds of thermochemical data, the gas-phase basicities were finally calculated. Before entering into the details of these calculations, the structural aspect of the protonation of **1**−**3** will first be presented.

1,2-Ethanediamine, 1. Conformational analysis of neutral 1,2-ethylenediamine, **1**, has been done previously using ab initio molecular orbital calculations[11] and molecular mechanics calculations.[12] Structural parameters were also deduced from electron diffraction or microwave spectroscopy.[11d] Ten conformers have been characterized computationally in an energy range of ca. 15 kJ/mol.[11] The most stable structures have a gauche NCCN arrangement, in agreement with the experimental results. The most stable conformation corresponds to a gauche orientation of the substituents on the three bonds of the NCCN skeleton; it presents also an internal hydrogen bond (structure **1**gGg′, Figure 1). The **1**gAg′ conformer, which corresponds to the trans arrangement of the four heavy atoms, is situated 5 kJ/mol above **1**gGg′. This energy difference obviously includes the stabilization brought by the internal hydrogen bond, but also repulsive electrostatic and steric interactions as revealed by the

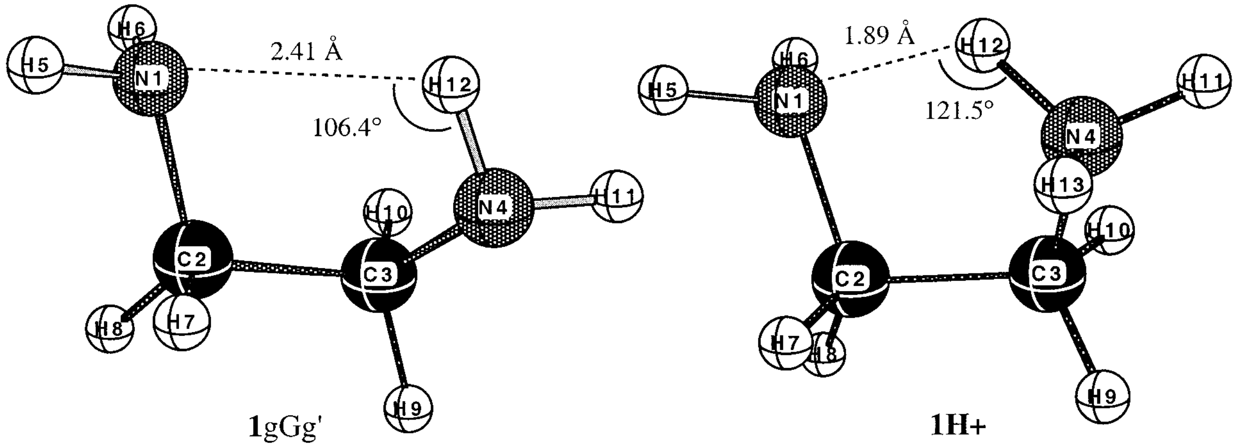

Figure 1. MP2/6-31G(d)-optimized geometry of the most stable conformers of 1,2-diaminoethane,**1**, and its protonated form, **1H**$^+$ (bond lengths in Å, bond angles in degrees).

TABLE 2: Entropy Calculation for the Neutral and Protonated Diamines 1−3

				$S°_t$[c]	
species	bond	V_0[a]	S° [b]	Pitzer	harmonic oscillator
1	N1−C2	16.1	325.8	14.53	10.79
	C2−C3	20.7		22.42	18.99
	C3−N4	16.1		14.47	10.84
1H$^+$	N1−C2	65.5	309.0	7.8	5.45
	C2−C3	54.8		18.7	15.42
	C3−N4	15.5		7.86	4.44
2	N1−C2	17.9	364.6	14.1	10.42
	C2−C3	22.0		23.9	20.53
	C3−C4	22.0		23.9	20.55
	C4−N5	17.1		14.1	10.64
2H$^+$	N1−C2	76.6	336.4	5.02	5.02
	C2−C3	77.5		15.53	15.53
	C3−C4	55.6		20.3	17.35
	C4−N5	18.3		7.1	4.02
3	N1−C2	27.2	406.3	12.0	8.81
	C2−C3	24.5		23.9	20.59
	C3−C4	12.0		30.8	26.51
	C4−C5	22.2		25.2	20.97
	C5−N6	27.2		12.0	8.87
3H$^+$	N1−C2	108.0	359.9	3.96	3.96
	C2−C3	91.2		15.23	15.23
	C3−C4	71.6		19.4	19.39
	C4−C5	71.7		16.75	16.75
	C5−N6	33.8		4.5	2.37

[a] Potential energy barrier of the internal rotation around the "bond"; value in kilojoules per mole, calculated at the HF/6-31G(d) level. [b] Total calculated entropy ($J{\cdot}mol^{-1}{\cdot}K^{-1}$) of the species considered. [c] Contribution to the entropy of the torsional modes calculated using Pitzer's procedure or within the harmonic oscillator approximation.

value of the CH_3NH_2-----NH_2CH_3 intermolecular hydrogen bond (22 kJ/mol; MP2/6-31G(d) calculation).

Rotations around the three CN and CC bonds of **1** have been investigated at the HF/6-31G(d) level to estimate the corresponding rotational barriers. Rotation of the NH_2 group in which the nitrogen atom is involved as a base in the internal hydrogen bond was explored by scanning the dihedral angle H(5)N(1)-C(2)C(3) (Figure 1). A pronounced maximum is observed in the potential energy profile for a value of the dihedral angle equal to 0°. At this point, the internal hydrogen bond is clearly broken and the calculated energy barrier is equal to 16 kJ/mol (Table 2). Considering now the rotation around the CC bond, the rotational barrier of 21 kJ/mol corresponds to the eclipsed conformer having a dihedral NCCN angle of zero degree. Similar values have been obtained at various levels of theory.[11] Moreover, the inclusion of electron correlation seems not to change the barrier height to an extent sufficient to induce large entropy variation. For example, an increase of 2 kJ/mol has been observed by Kim et al[11c] for the C(2)C(3) rotational barrier when passing from HF to MP2/6-31G(d,p) levels. This corresponds to a negligibly small entropy difference of 0.4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ in the harmonic oscillator approximation. Finally, the rotation of the second NH_2 group was explored by scanning the dihedral angle H(11)N(4)C(3)C(2) (Figure 1). The overall barrier for this rotation is in fact identical with that obtained previously when considering the other amino group (16 kJ/mol). The comparison between these three energy barriers and the difference in energy between **1**gAg′ and **1**gGg′ conformers reveals that most of the torsional critical energy is brought by repulsive interactions between eclipsed substituents rather than the breaking of the internal hydrogen bond.

The most stable form of protonated 1,2-ethanediamine, **1H**$^+$, allows the formation of an internal hydrogen bond. At the MP2/6-31G(d) level, the N---H distance is approximately equal to 1.9 Å; the N---H−N bond angle and NCCN dihedral angle are equal to 121.5° and 44.6°, respectively (Figure 1). These results are in correct agreement with previous calculations conducted at a lower theoretical level.[13] Dipole−dipole interactions and steric constraints limit the extent of the internal hydrogen bond. A rough estimate of its strength may be given by the energy difference between **1H**$^+$ and the full anti structure. The difference, which amounts to 48 kJ/mol at the MP2(FC)/6-31G* + ZPE level, is well below the complexation energy of 91 kJ/mol determined for the bimolecular system CH_3NH_2 + $CH_3NH_3^+$[15] as expected for a constrained internal hydrogen bond.

Rotational barriers around the N(1)−C(2) and the C(2)−C(3) bonds are as high as 65 and 55 kJ/mol, respectively. The transition structures are eclipsed conformers in which the internal hydrogen bond is clearly broken. By contrast, the rotation of the NH_3 group around the C(3)−N(4) bond presents a barrier height of only 15 kJ/mol and a 3-fold symmetry. This low energy barrier occurs because the NH_3 group can rotate while maintaining one (or two) favorable interactions between one (or two) H of the NH_3 group and the lone pair of the second nitrogen atom. No complete breaking of the internal hydrogen bond is thus occurring during the rotation around the C(3)−N(4) bond.

1,3-Propanediamine, 2. Conformational analysis of neutral 1,3-propanediamine, **2**, has been done by means of ab initio molecular orbital calculation[11b] and by molecular mechanics MM2 method.[12b] The most stable of the 25 conformers identified

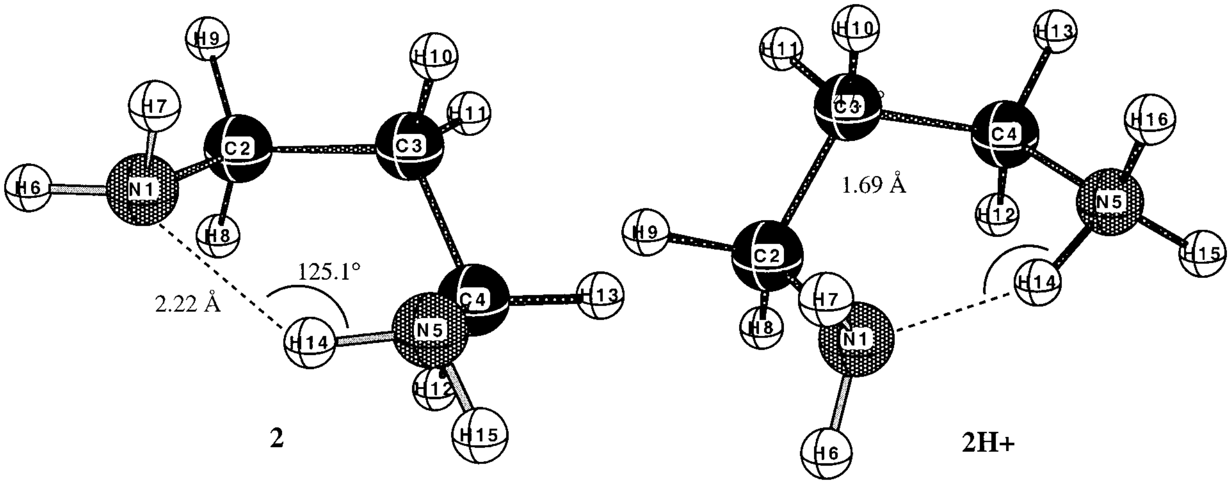

Figure 2. MP2/6-31G(d)-optimized geometry of the most stable conformers of 1,3-diaminopropane, **2**, and its protonated form, **2H**$^+$ (bond lengths in Å, bond angles in degrees).

by Bultinck et al.[11b] possesses a gauche NCCC arrangement allowing the formation of an internal hydrogen bond (**2**, Figure 2). At the MP2/6-31G(d) level the H---N distance is equal to 2.22 Å. The conformer for which the bonds participating in the NCCCN frame are all in the anti conformation is situated 6 kJ/mol above 2 [HF/6-31g(d) level]. The internal hydrogen bond in **2** consequently has strength similar to that in 1,2-ethanediamine, **1**.

Investigation of the various torsional modes reveals energy barriers in the range 17−22 kJ/mol. In all cases the transition structures correspond to eclipsed conformations. These characteristics, comparable with **1**, indicate again that the barriers for internal rotation arise essentially from eclipsed repulsive interactions.

The protonated 1,3-propanediamine, **2H**$^+$**,** in its most stable conformation presents also a cyclic arrangement of its heavy atoms. The geometrical parameters obtained at the MP2/6-31G(d) level are indicated in Figure 2. They are similar to the HF/3-21G results.[13a] The length of the hydrogen bond is 1.69 Å, and the bond angle N---H−N is approximately 148°. When compared with the protonated ethanediamine, **1H**$^+$, the N---H−N angle is larger and the N---H distance is shorter. The internal hydrogen bond is thus stronger in **2H**$^+$. Another proof is provided by the stabilization energy of this conformation. Accordingly, the conformer of the protonated 1,3-propanediamine where the NCCCN atoms are in their anti conformation is 75 kJ/mol above **2H**$^+$. This difference is more important here than in the protonated ethanediamine (48 kJ/mol) and nearest to the stabilization energy of the protonated dimer $(CH_3NH_2)_2H^+$ (91 kJ/mol, ref 15).

The rotational barriers around the N(1)C(2) and C(2)C(3) bonds reflect the 75 kJ/mol necessary to break the internal hydrogen bond. Rotation around the C(3)C(4) bond shows a less pronounced barrier height, because the CCCN anti conformation allows a favorable interaction between the nitrogen atom N(1) and the (positively charged) carbon atom C(4) in the transition structure. This stabilizing effect reduces the corresponding energy barrier.

As observed for protonated 1,2-ethanediamine, the rotation of the NH_3 group around the C(4)N(5) bond preserves an internal hydrogen bonding. The corresponding potential energy profile exhibits three minima during a complete revolution and identical barriers of 18.3 kJ/mol.

1,4-Butanediamine, 3. It was not in the scope of the present work to investigate all the possible conformers of 1,4-butanediamine. However, many of them were located during the search for the rotational barriers associated with the torsional modes. One of the most stable form of **3** presents a chair conformation that allows the formation of an internal hydrogen bond, as already observed for **1** and **2**. The values of the optimized geometrical parameters obtained at the MP2/6-31G(d) level for this conformer are indicated in Figure 3. Others conformers of comparable stability, but without internal hydrogen bonds, correspond to anti conformations of the N(1)C(2)C(3)C(4), C(2)C(3)C(4)C(5), or C(3)C(4)C(5)N(6) frames. In fact, as also noted for **1** and **2**, the steric and electrostatic repulsions are more important than the internal hydrogen bond stabilization energy. The rotational energy barriers, which range from 12 to 27 kJ/mol, correspond essentially to the repulsions of the various substituents in eclipsed transition structures.

The most stable form of protonated 1,4-butanediamine is clearly the conformer **3H**$^+$ depicted in Figure 3. As expected, the internal hydrogen bond (1.59 Å) is shortened with respect to the lower homologues **1H**$^+$ (1.89 Å) and **2H**$^+$ (1.69 Å). The N−H---N angle is also larger (approximately 164°). The situation is close to a linear arrangement of the three atoms participating to the internal hydrogen bond. Consequently, the stabilization energy is larger for **3H**$^+$ than for **1H**$^+$ or **2H**$^+$. The value, as estimated by the energy difference between **3H**$^+$ and the full anti conformer, is equal to 85 kJ/mol (MP2/6-31G*//HF/6-31G* + ZPE level). It is not far from the complexation energy of the protonated dimer $(CH_3NH_2)_2H^+$ (91 kJ/mol, ref 15).

The rotations around the different bonds of the N(1)C(2)-C(3)C(4)C(5) system are characterized by high energy barriers (from 72 to 108 kJ/mol) in agreement with the high strength of the internal hydrogen bond in **3H**$^+$. The rotation of the $N(6)H_3$ group is again associated with a small barrier of 34 kJ/mol because of the persistence of an hydrogen bonding during the rotation.

Protonation Thermochemistry. During the entropy calculations, it has been generally observed that most of the entropy difference $\Delta S°_p = S°(MH^+) - S°(M)$ is coming from the entropy terms associated with the internal rotations. Calculation of the relevant contributions to $S°$ by the Pitzer's method uses corrective terms that are dependent on the rotational barrier height V_0.[10] When this barrier exceeds ca. 50 kJ/mol (i.e., 20 RT at 298 K), the $S°$ term is close to that which is calculated using the harmonic oscillator approximation. (The difference is less than 0.5 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.) For the neutral diamines **1**−**3**

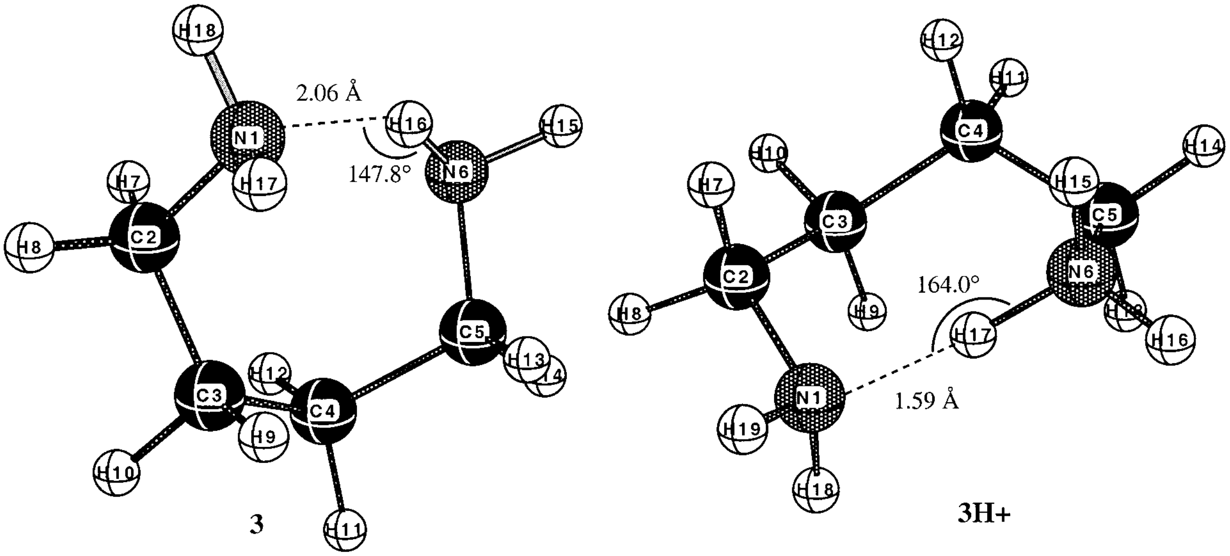

Figure 3. MP2/6-31G(d)-optimized geometry of the conformers of 1,4-diaminobutane, **3**, and its protonated form, **3H**$^+$ (bond lengths in Å, bond angles in degrees).

TABLE 3: Summary of Basicity Calculations for Diamines 1−3

	H°_{298}[a] (Hartree)	$\Delta_f H^\circ_{298(\mathrm{calc})}$[a] (kJ/mol)	$\Delta_f H^\circ_{298(\mathrm{exp})}$[b] (kJ/mol)	PA(M)[a] (kJ/mol)	ΔS^0_p[c] ($J{\cdot}mol^{-1}{\cdot}K^{-1}$)	GB(M)[d] (kJ/mol)
1	−190.149054	−18.1	−17.6	947.7	−16.8	910.3 (912.4)
1H$^+$	−190.507659	565.1				
2	−229.371550	−35.6	(35.7)	977.7	−29.2	936.9 (940.0)
2H$^+$	−229.74134	518.1				
3	−268.592645	−49.7	(56.3)	999.8	−46.4	953.6 (954.4)
3H$^+$	−268.971118	481.2				

[a] Calculated G2(MP2) results. [b] Experimental values from ref 17 for **1**; calculated using the incremental method of Benson[18] for **2** and **3**. [c] $\Delta S^\circ_p = S^\circ(\mathrm{MH^+}) - S^\circ(\mathrm{M})$ with $S^\circ(\mathrm{MH^+})$ and $S^\circ(\mathrm{M})$ presented in Table 2. [d] Calculated using $\mathrm{GB(M)} = \mathrm{PA(M)} - T\,[\Delta S^\circ_p - S^\circ_{\mathrm{H^+}}]$; the experimental values are given in parentheses (see Table 1 for details).

the rotational barrier height is situated between 12 and 27 kJ/mol, and the use of the Pitzer's approach was necessary to estimate $S^\circ(\mathrm{M})$ at 298 K. In the protonated species, **1H**$^+$−**3H**$^+$, the rotational barriers are generally larger than 60 kJ/mol and the harmonic oscillator approximation works correctly. As observed above, the only exception is the rotation of the NH_3 group, which may occur without a complete breaking of the internal hydrogen bond. For this latter torsional mode, the rotational barrier is situated between 15 and 34 kJ/mol and the symmetry number is equal to 3. In that case again, Pitzer's method has been used to estimate its entropic participation. The individual contributions to entropy of each torsional modes, S°_t, estimated using the Pitzer model and the harmonic oscillator approximation (using eq 3 and 5), are presented in Table 2.

As expected from equations 3 and 5, the S°_t terms associated with the torsional modes are dependent on the barrier height V_0 and the reduced moment of inertia I_{red}. An increase of V_0 is associated with a decrease of S°_t, as clearly illustrated for a given torsion by a comparison between the S°_t of the neutral and the protonated forms. The role of the reduced moment of inertia is to decrease the S°_t value of the torsion involving the bonds to the one closest to the extremities of the molecule.

For the three species, the contribution to the entropy difference ΔS°_p associated with the rotation of the amino group bearing the proton is close to a common value of -7 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. As long as the corresponding rotational barriers are approximately the same in both the neutral and the protonated forms, this contribution to ΔS°_p is mainly due to the symmetry change of this torsional mode during protonation. Considering now the rotations that are hindered after the protonation, for the three investigated molecules, each individual contribution to ΔS°_p for hindered rotations falls between -4 and -11 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. This entropy loss is obviously related to the large increase of the rotational barrier when passing from the neutral to the protonated structures. For example, for the N(1)C(2) rotation, V_0 passes from 16.0 kJ/mol in **1**, to 65.5 kJ/mol in **1H**$^+$. The barrier height is increased by a factor of 4, and consequently the corresponding harmonic frequency is increased by a factor 2 (from 160 to 320 cm^{-1}). This corresponds to an entropy loss of -6.7 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

The net result of the hindrance of the torsional modes is a clear decrease of the entropy difference ΔS°_p when the size of the molecule increases (Table 3). This corroborates the experimental observations.[2,3] The calculated entropy difference, ΔS°_p, is in correct agreement with the experimental estimate of Mautner et al.[3] for **1** (calculated $\Delta S^\circ_p = -16.8$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ compared with the experimental value of -22.1 $J{\cdot}K^{-1}{\cdot}mol^{-1}$). However, for **2** and **3**, the absolute values of the calculated ΔS°_p (-29.2 and -46.4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, respectively) are below the experimental values of Mautner et al.[3] by 20 and 15 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, respectively.

Turning now to the enthalpic quantities, the 298 K heats of formation values calculated via atomization reactions (eqs 1 and 2) at the G2(MP2) level are also indicated in Table 3. When a comparison with experiment is possible, that is, for the neutral molecule **1**, the agreement is excellent. A similar observation is made for molecule **2** when using Benson's incremental method in estimating $\Delta_f H^\circ_{298}(\mathbf{2})$, but a significant deviation is observed for molecule **3**. The proton affinity values quoted in Table 3 have been calculated using the G2(MP2) H_{298} values of M and MH^+ and the enthalpy of translation of the proton. It can be seen that the G2(MP2) calculated values are systematically lower than the tabulated ones (ref 4, Table 1); the difference amounts to 3.9, 9.3, and 5.8 kJ/mol for **1**, **2** and **3**, respectively. This difference is obviously dependent on the choice of the ΔS°_p values used in the expression $PA(M) = GB(M) + T\,[\Delta S^\circ_p - S^\circ_{H^+}]$. If one considers that G2 theory generally leads to proton affinities in agreement with experimental values to within ±5kJ/mol,[9c] our results suggest that the ΔS°_p values selected in ref 4 (Table 1) are too negative.

Finally, combining the calculated proton affinities and ΔS°_p, gas-phase basicity estimates may be proposed. The GB(M) obtained by this means (Table 3) are in excellent agreement with the experimental values (Table 1) for which a clear consensus has been observed. In fact, the deviation between theory and experiment is comparable with the experimental uncertainty (i.e., 2 kJ/mol, see Table 1). This further corroborates the correct estimate of the ΔS°_p term by the method described in this study.

Conclusion

In summary, the protonation thermochemistry of alkyldiamines M = **1**−**3** has been examined using ab initio molecular orbital calculations for the estimate of the entropy contribution $\Delta S^\circ_p = S^\circ(MH^+) - S^\circ(M)$ and the proton affinity, PA(M). For the first time, the entropy calculation, although approximate, explicitly takes into account the locking of the internal rotations during the protonation. A model based on Pitzer's method has been used to calculate the S° terms associated with internal rotations in the neutral and protonated forms of alkyldiamines **1**−**3**. The proton affinities of these molecules were computed at the well-established G2(MP2) level.

When possible, the comparison between theory and experiment is excellent. This is, for example, the case of the third law entropy and heats of formation values which, for the neutral molecules, show deviations of less than 4 $J\cdot K^{-1}\cdot mol^{-1}$ and 6 kJ/mol, respectively. Moreover, the combination of the calculated proton affinities and ΔS°_p leads to excellent estimates of the gas-phase basicities GB(M) (maximum deviation ≈2 kJ/mol). This suggests that the ΔS°_p terms and the PA values are correctly estimated by the calculations. However, small discrepancies appearing between theory and experiment for ΔS°_p remain to be to be explained.

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