

Neutral Intramolecular Hydrogen-Bonded Bases*

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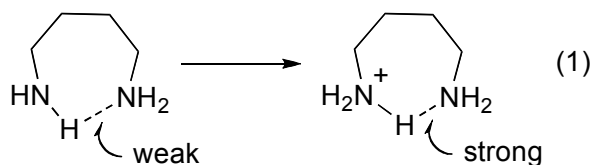
Abstract. B3LYP/aug-cc-pVDZ computations were carried out on polyamines with up to seven amino groups. The gas-phase proton affinities of these compounds are 219.6 (1-BuNH₂), 238.6 (H₂NCH₂CH₂CH₂CH₂NH₂), 252.8 [(H₂NCH₂CH₂CH₂)₂CHNH₂], 261.3 [(H₂NCH₂CH₂CH₂)₃CNH₂ (**1**)], and 288.5 kcal mol⁻¹ [(H₂NCH₂CH₂CH(NH₂)CH₂CH₂)₃CNH₂]. These results indicate that the tetraamine is near the top of the basicity scale and the heptaamine is more basic than any neutral organic compound which has been measured to date. A gas-phase equilibrium acidity determination between **1** and DBU also was carried out, and PA(**1**) = 256.2 ± 2.1 kcal mol⁻¹ was obtained. This demonstrates that multiple intramolecular hydrogen bonds can greatly increase basicities, and represents a new motif for designing super bases.

Keywords: super bases, gas-phase basicity, hydrogen-bonding, computations

INTRODUCTION

Proton transfer and base-catalyzed reactions are widely encountered processes in chemistry. As a result, the development of new and powerful bases is an on going effort. Maksić and coworkers have discovered a variety of super bases in the gas-phase using computations, and have reported a number of motifs for making such species.¹⁻²⁵ Experimental studies on related neutral organic compounds by Koppel,²⁶⁻²⁸ Gal,^{29,30} Bouchoux,^{31,32} Kebarle,³³⁻³⁵ and others have extended the gas-phase proton affinity scale (ΔH°) so that it now spans a ~150 kcal mol⁻¹ range from 126.5 (CF₄) to 272.8 (EtN=P(NMe₂)₂N=P(NMe₂)₃) kcal mol⁻¹.^{27,36-43} Amines are in the upper half of this range (e.g., the proton affinities of NH₃ and NMe₃ are 204.0 and 226.8 kcal mol⁻¹, respectively) and diamines are even more basic. For example, the proton affinity of butane-1,4-diamine is 240.3 kcal mol⁻¹, and this can readily be explained as being the result of an internal hydrogen bond. That is, the ammonium ion is stabilized by an intramolecular hydrogen bond which is much stronger than in the conjugate base (Eq. (1)), thereby leading to an enhanced basicity.

In this paper, we examine the consequences of multiple intramolecular hydrogen bonds on the proton affinities of primary polyamines as a new design element for enhancing basicity. The results of density func-



tional theory calculations are reported herein as is the experimental gas-phase proton affinity of a tetraamine, 4-(3-aminopropyl)heptane-1,4,7-triamine [(H₂NCH₂CH₂CH₂)₃CNH₂] (**1**).

EXPERIMENTAL

Gas-Phase Experiments

A 3 T Fourier transform mass spectrometer (FTMS) equipped with a dual cell and an IonSpec Co. (now Varian) data system running Omega 8.0.309. was used to measure the gas-phase basicity of (H₂NCH₂CH₂CH₂)₃CNH₂ (**1**). This quantity was bracketed initially with standard reference bases in both directions, and then the equilibrium constant with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was determined by measuring the forward and reverse proton transfer rate constants. To accomplish this, the pressure of **1** in the reaction region was needed to obtain the rate constant

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

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with protonated DBU (DBUH⁺). This quantity is difficult to determine because (H₂NCH₂CH₂CH₂)₃CNH₂ is not very volatile and had to be added into the instrument *via* the solid probe inlet. A pressure differential results since the sample is introduced ~1 cm from the reaction region but ~1 m from the ionization gauge used to measure the pressure. To correct for this imbalance, the reaction rates of the tetraamine with DBUH⁺ and NH₄⁺ were measured in rapid succession. The latter process is very exothermic, so it can be assumed to occur at the collision rate.⁴⁴ This enabled the pressure of **1** and the rate constant for the reaction with DBUH⁺ to be determined.

Synthesis

4-(3-Aminopropyl)-4-nitroheptane-1,7-diamine (**3**)

To a solution of 12.0 g (54.5 mmol) of tris(β-cyanoethyl)nitromethane (**2**)⁴⁵ in 750 ml of dry THF at ambient temperature was added 200 ml (200 mmol) of a 1.0 M solution of borane in THF. After the addition was completed, the reaction mixture was refluxed for 15 hrs. The resulting gelatinous mass was cooled to 10 °C, and cold 10 % HCl was slowly added until the mixture became fluid and had an acidic pH. The resulting solution was stirred with a mechanical stirrer for 1 hr, and then was made basic with a saturated solution of sodium carbonate. It was subsequently evaporated to dryness with a rotary evaporator at aspirator pressure and further dried under full vacuum with a mechanical pump.

The residue was triturated with hot absolute ethanol (4 × 500 ml) and each portion was quickly filtered under a positive pressure of nitrogen through a short (5 cm) celite pad with a diameter of 5 cm. Upon removal of the solvent, the crude 4-(3-aminopropyl)-4-nitroheptane-1,7-diamine (**3**) was dissolved in methanol containing an excess of 3 % HCl to give the hydrochloride salt. The water and methanol were evaporated using a rotary evaporator and then a mechanical pump, and the resulting salt (16.0 g) was used in the next step without any additional purification. **3** (HCl salt): ¹H NMR (300 MHz, D₂O) δ/ppm: 2.88 (t, 6H, *J* = 7.5 Hz), 1.93 (m, 6H), 1.48 (m, 6H); ¹³C NMR (75 MHz, CD₃OD) δ/ppm: 93.6, 39.0, 31.4, 21.2.

4-(3-Aminopropyl)heptane-1,4,7-triamine (**1**)

The crude hydrochloride salt of **3** from the previous step (16.0 g) was dissolved in a MeOH (200 ml)/H₂O (40 ml) mixture and 2.0 g of a water slurry of Raney-nickel (W. R. Grace and Co. Raney 2800 from Sigma-Aldrich) was added. This mixture was shaken for 72 hrs at room temperature under atmospheric pressure to carry out the hydrogenation. It was subsequently filtered through short pad of celite and 50 ml of 3 % HCl in methanol was added. The reaction mixture was concentrated to a smaller volume (≈30 ml) and loaded onto a 50 × 3.5 cm

column containing 230 g of Dowex Marathon A2 anion-exchange resin (30–40 mesh) in its OH⁻ form, which had been prewashed with methanol to remove water. The product was eluted with anhydrous methanol until pH paper indicated that the pH of the eluent was neutral. Evaporation of the solvent and drying of the residue afforded a liquid which was distilled at 160 °C at 10⁻⁵ torr to give 7.01 g (64 % for the two steps) of 4-(3-aminopropyl)heptane-1,4,7-triamine (**1**). Hydrochloride salt: ¹H NMR (300 MHz, CD₃OD) δ/ppm: 2.94 (br. s, 6H), 1.79 (br. s, 12H); ¹³C NMR (75 MHz, CD₃OD) δ/ppm: 59.3, 40.6, 33.9, 22.3. Free base: ¹H NMR (300 MHz, CD₃OD) δ/ppm: 2.60 (t, 6H, *J* = 6.5 Hz), 1.39 (m, 12H); ¹³C NMR (75 MHz, CD₃OD) δ/ppm: 54.1, 43.5, 38.1, 28.1. HR FTMS (ESI) calcd. for C₁₀H₂₇N₄ (M+H)⁺: 203.2230; found: 203.2244.

Calculations

Computations were carried out using the Becke three-parameter hybrid exchange and Lee-Yang-Parr correlation density functional (*i.e.*, B3LYP)^{46,47} along with Dunning's augmented correlation-consistent double-ζ basis set (*i.e.*, aug-cc-pVDZ)⁴⁸ as implemented in Gaussian 03.⁴⁹ Full geometry optimizations were carried out on 10 or more conformations of (H₂NCH₂CH₂-CH₂)₂CHNH₂ and (H₂NCH₂CH₂CH₂)₃CNH₂ using IBM and SGI workstations at the Minnesota Supercomputer Institute after generating initial conformational sets *via* Monte Carlo calculations with the MMFF force field using Spartan 04.⁵⁰ Vibrational frequencies were subsequently computed for the optimized structures and no scaling factor was used in calculating the zero-point energies and thermal corrections to 298 K. In the latter case, however, frequencies which contributed more than (1/2)*RT* were replaced by (1/2)*RT*. All of the resulting energies are given as enthalpies at 298 K unless otherwise specified.

RESULTS AND DISCUSSION

Geometry optimizations were carried out on 1-butanamine, butane-1,4-diamine, heptane-1,4,7-triamine, 4-(3-propylamine)heptane-1,4,7-triamine (**1**), and their conjugate acids. Protonation preferentially occurs at the internal amino group in the latter two compounds and these two ammonium ions have two and three intramolecular hydrogen bonds, respectively, (Figure 1). This ties up all of the acidic sites in the conjugate acid of **1**, which should increase its stability relative to the other ammonium ions. To address this issue further, the proton affinities of the four amines were computed (Table 1).

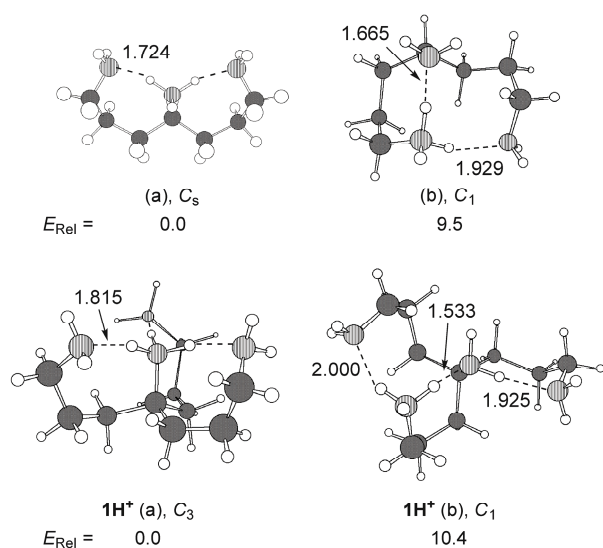
1-Butanamine is predicted to have a proton affinity of 219.6 kcal mol⁻¹, which is in excellent accord with

Table 1. Calculated B3LYP/aug-cc-pVDZ proton affinities of a series of amines (298 K)

Compound	PA kcal mol ⁻¹		Δ PA ^(a) kcal mol ⁻¹
	Calcd.	Expt.	
CH ₃ CH ₂ CH ₂ CH ₂ NH ₂	219.6	220.2 ± 2.0 ^(b)	-
H ₂ NCH ₂ CH ₂ CH ₂ CH ₂ NH ₂	238.6	240.3 ± 2.0 ^(b)	19.0
(H ₂ NCH ₂ CH ₂ CH ₂) ₂ CHNH ₂	252.8		33.2
(H ₂ NCH ₂ CH ₂ CH ₂) ₃ CNH ₂	261.3	256.2 ± 2.1	41.7
(H ₂ NCH ₂ CH ₂ CH(NH ₂)- CH ₂ CH ₂) ₃ CNH ₂	288.5		68.9

^(a) Δ PA = PA(RNH₂) - PA(1-BuNH₂).^(b) See reference 42.

the experimental value of 220.2 ± 2.0 kcal mol⁻¹. Substitution of a δ -hydrogen with an amino group leads to a 19.0 kcal mol⁻¹ increase in the basicity, and the predicted value is again in very good agreement with experiment. Incorporation of a third and fourth amino group by successive substitution of the α -hydrogens in butane-1,4-diamine with a 3-aminopropyl group (*i.e.*, H₂NCH₂-CH₂CH₂-) leads to proton affinities of 252.8 and 261.3 kcal mol⁻¹ for the triamine and the tetraamine, respectively. These increases in the proton affinities correspond to enhancements of 33.2 and 41.7 kcal mol⁻¹, respectively, relative to 1-butanamine. These results can be attributed to the greater number of hydrogen bonds at the ammonium ion centers. The latter proton affinity also is predicted to be somewhat greater than that for Me₂NC(CH₃)=NCH₂CH₂CH₂NMe₂ (PA = 257.5 kcal mol⁻¹), which until recently was at the top of the gas-phase basicity scale. This despite the fact that **1** is a

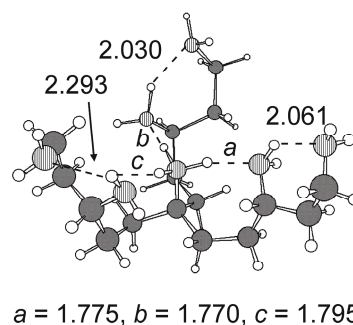
**Figure 1.** B3LYP/aug-cc-pVDZ structures of protonated 1,4,7-triaminoheptane and 4-(3-propylamine)-1,4,7-triaminoheptane (**1H**⁺) at both basic sites along with their relative energies. The energies are given in kcal mol⁻¹ at 298 K.

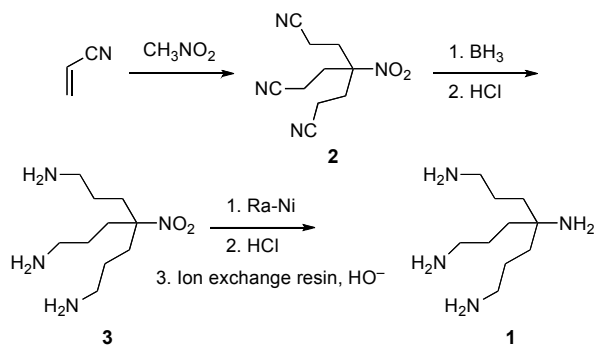
saturated compound containing only C, N, and H whereas all of the organic bases with measured proton affinities in excess of 250 kcal mol⁻¹ are unsaturated except for two Verkade bases whose conjugate acids are stabilized by resonance.²⁷

Given the additive nature of the intramolecular hydrogen bonds on the proton affinities, and that **1H**⁺ can be viewed as having a complete first-solvation shell, a heptaamine which can have a second solvation shell was explored. 6-(5-Pentyl-1,3-diamine)undecane-1,3,6,9,11-pentaamine [(H₂NCH₂CH₂CH(NH₂)-CH₂CH₂)₃CNH₂] (**4**) was chosen because of its conformational flexibility, but a detailed conformational analysis was not carried out for the same reason. A protonated structure with six intramolecular hydrogen bonds (**4H**⁺), however, was readily located (Figure 2). Each of the hydrogens at the ammonium ion center is involved in a hydrogen bond, the primary solvation shell. The three amino groups which serve as the hydrogen bond acceptors also act as hydrogen bond donors (*i.e.*, the second solvation shell). This results in the charge being delocalized over a large area and leads to stabilization of the ion. As a result, the computed proton affinity of **4** is a remarkable 288.5 kcal mol⁻¹ (Table 1), which corresponds to a 68.9 kcal mol⁻¹ enhancement relative to the basicity of 1-butanamine. It also suggests that **4** is a stronger neutral organic base than any other such compound which has been measured to date (*i.e.* its basicity is predicted to be off-scale).

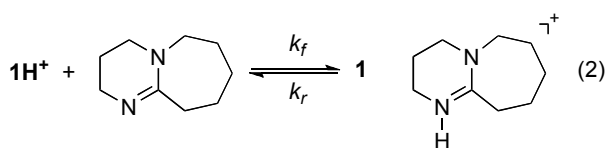
To test the computed results, we decided to measure the proton affinity of tetraamine **1**. This compound has not been reported previously, however, so it had to be synthesized. This was accomplished in two steps from tris(β -cyanoethyl)nitromethane (**2**),⁴⁵ which is known, and three steps overall as shown in Scheme 1. The proton affinity of **1** was subsequently measured by a gas-phase equilibrium determination with diazabicyclo[5.4.0]undec-7-ene (DBU).

The forward and reverse rate constants for the acid-base reactions shown in Eq. (2) were measured to obtain the equilibrium constant since $K = k_f/k_r$. Both rate

**Figure 2.** A B3LYP/aug-cc-pVDZ optimized geometry of protonated 6-(5-pentyl-1,3-diamine)undecane-1,3,6,9,11-pentaamine (**4H**⁺).



Scheme 1. Synthesis of tetraamine 1.



constants were independently measured three times to afford $k_f = (1.55 \pm 0.23) \times 10^{-10}$ and $k_r = (2.74 \pm 0.02) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This leads to $K = 0.57 \pm 0.08$ and a gas-phase basicity (GB) difference of $0.3 \pm 0.5 \text{ kcal mol}^{-1}$, where an uncertainty of $\pm 100\%$ in the equilibrium constant was adopted for deriving the error limit in ΔGB . The absolute basicity of DBU is $242.7 \pm 2.0 \text{ kcal mol}^{-1}$ which enables $\text{GB}(\mathbf{1}) = 243.0 \pm 2.1 \text{ kcal mol}^{-1}$ to be assigned. In order to convert this free energy into an enthalpy and obtain the proton affinity, the entropy of $\mathbf{1}$ and $\mathbf{1H}^+$ are needed. These quantities (141.9 and 124.0 e.u., respectively) were computed by using unscaled B3LYP/aug-cc-pVDZ vibrational frequencies, but in the former case seven low energy conformations were found to have significant populations ($\geq 8\%$). In this instance the entropy was determined by weighting each conformer based upon a Maxwell Boltzmann distribution. This complication has little impact upon the final result, however, since all of the structures have entropies within 0.5 e.u. of each other. The overall entropy for the deprotonation of $\mathbf{1H}^+$ is a rather large $43.9 \text{ cal mol}^{-1} \text{ K}^{-1}$, but this is not surprising given the flexibility of $\mathbf{1}$ and the presence of multiple hydrogen bonds in $\mathbf{1H}^+$.³⁹ In any case, if an uncertainty of ± 2 e.u. is assumed, then $\text{PA}(\mathbf{1}) = 256.2 \pm 2.2 \text{ kcal mol}^{-1}$ is obtained. This value is a little smaller than expected based upon the B3LYP results, but the DFT prediction is in reasonable accord with experiment if one accounts for the experimental uncertainty in the proton affinity.

CONCLUSION

4-(3-Propylamine)heptane-1,4,7-triamine is the most basic amine measured to date. It also is near the top-end of the gas-phase basicity scale even though it is a prima-

ry amine and it's well known that the basicity at nitrogen increases with increasing alkyl substitution (*i.e.* $\text{PA}(\text{NH}_3) = 204.0 < \text{PA}(\text{CH}_3\text{NH}_2) = 214.9 < \text{PA}((\text{CH}_3)_2\text{NH}) = 222.2 < \text{PA}((\text{CH}_3)_3\text{N}) = 226.8 \text{ kcal mol}^{-1}$). This demonstrates that multiple intramolecular hydrogen bonds can increase basicities markedly. Moreover, these compounds should also be basic in non-protic solvents, and thus are apt to be synthetically useful. We therefore intend to explore the basicities and reactivities of polyamines in condensed media.

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Neutralne baze sa intramolekularnom vodikovom vezom

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Provedeni su B3LYP/aug-cc-pVDZ računi poliamina koji sadrže do sedam amino skupina. Protoski afiniteti u plinskoj fazi ovih spojeva su 219.6 (1-BuNH₂), 238.6 (H₂NCH₂CH₂CH₂CH₂NH₂), 252.8 [(H₂NCH₂CH₂CH₂)₂CH-NH₂], 261.3 [(H₂NCH₂CH₂CH₂)₃CNH₂ (**1**)] i 288.5 kcal mol⁻¹ [(H₂NCH₂CH₂CH(NH₂)CH₂CH₂)₃CNH₂]. Ovi rezultati ukazuju da je tetraamin blizu vrha skale bazičnosti, heptaamin je bazičniji od bilo koje druge do sada mjerene neutralne organske molekule. Također je određena ravnotežna kiselost u plinskoj fazi između **1** i DBU, te dobiven PA(**1**) = 256.2 ± 2.1 kcal mol⁻¹. Rezultati pokazuju kako višestruke intramolekularne vodikove veze mogu znatno povećati bazičnost, te predstavlja novi strukturalni motiv za dizajn superbaza.