

These were also identified by the relative sizes of the vicinal ^{13}C - ^{13}C coupling constants. To confirm the structure of the diastereomers **2** and **3** the C7-position was ^{13}C enriched (**2b** and **3b**) to observe the vicinal coupling constants to C2 and C3; the results for the dilabeled compound **2b**, **3b**, and **9b** are given in Table III.

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Supplementary Material Available: Tables of calculated INDO FPT MO results for vicinal ^1H - ^1H and ^{13}C - ^{13}C coupling constants in **1**, ^{13}C - ^{13}C coupling constants in **2**, and ^{13}C - ^{13}C coupling constants in **4** (4 pages). Ordering information is given on any current masthead page.

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Site of Protonation and Conformational Effects on Gas-Phase Basicity in β -Amino Alcohols. The Nature of Internal H Bonding in β -Hydroxy Ammonium Ions

Raymond Houriet,*† Hermann Rüfenacht,† Pierre-Alain Carrupt,† Pierre Vogel,† and Milos Tichý‡

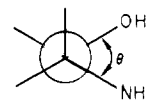
Contribution from the Institut Chimie Physique EPFL, 1015 Lausanne, Switzerland, Institut Chimie Organique de l'Université, 1005 Lausanne, Switzerland, and Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, 16610 Prague, Czechoslovakia. Received October 18, 1982

Abstract: The influence of interfunctional distance on the gas-phase basicity of β -amino alcohols is investigated by the method of equilibrium proton-transfer reactions in an ion cyclotron resonance (ICR) spectrometer. It is found that in the protonated species, interaction between the most basic center (amino group) with the hydroxy group results in stabilization of the system. The stabilization energy increases as the interfunctional distance decreases to reach a maximum value of about 7 kcal/mol for coplanar systems. Comparison with the values determined by ab initio calculations indicates that internal H bonding can be described in terms of the ion-dipole potential energy between the ammonium ion and the hydroxy group. External vs. internal ion solvation effects are also discussed.

The determination of basicity properties of isolated molecules is a rapidly expanding field of gas-phase chemistry. From the large number of data already accumulated on monofunctional compounds, a detailed picture of the effects of substituents has emerged (see ref 1 for a recent review). Useful comparisons can be made with the numerous solution results in order to evaluate the influence of solvation on molecular properties. Another challenge is provided by multifunctional systems in which one has to distinguish between different possible sites for protonation and thus different basicity values associated with each reaction site.²

The purpose of the present study is the determination of the gas-phase basicity (GB) of seven conformationally stable β -amino alcohols, compounds **1-7**, in which the dihedral angle θ (CO-CN)

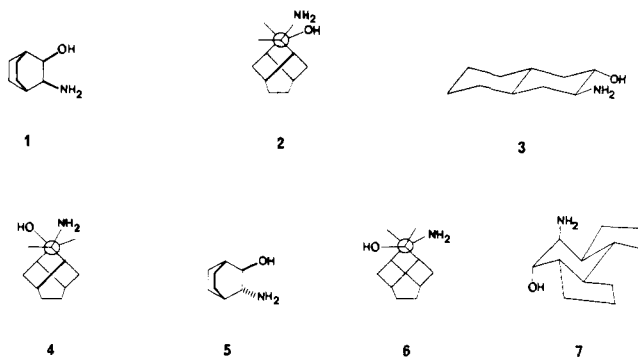
ranges from 0° to 180° , according to



- | | |
|------------------------|-------------------------|
| 1, $\theta = 0^\circ$ | 5, $\theta = 120^\circ$ |
| 2, $\theta = 30^\circ$ | 6, $\theta = 150^\circ$ |
| 3, $\theta = 60^\circ$ | 7, $\theta = 180^\circ$ |
| 4, $\theta = 90^\circ$ | |

In a previous investigation of the chemical ionization mass spectra of these compounds,³ it has been shown that there is a relationship between the interfunctional distance and the loss of water from the protonated amino alcohol. It was then found that water loss becomes significant only when $\theta \geq 120^\circ$, and these results suggested the possibility for internal proton transfer to form stable N-protonated species.

We want to establish quantitatively the gas-phase basicity of these compounds by the method of equilibrium proton transfer in an ion cyclotron resonance spectrometer (ICR)⁴ in order to determine first the site of protonation in these amino alcohols. Another question is related to the possibility for interaction be-



* Institut Chimie Physique.

† Institut Chimie Organique de l'Université.

‡ Institute of Organic Chemistry and Biochemistry.

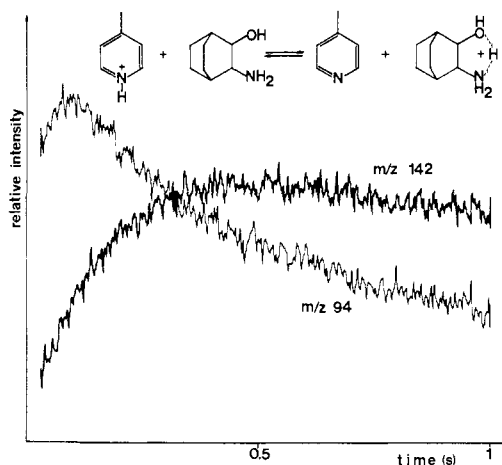


Figure 1. Time plot for the determination of the equilibrium constant for reaction 1 where AA = **1** (1.1×10^{-6} torr pressure) and B = 4-MPY (1.4×10^{-6} torr).

tween the two functional groups in the protonated species. A stabilizing interaction, i.e., formation of an internal H bond may be predicted on the basis of related studies on α,ω -bifunctional alkane derivatives.⁵ We are thus interested in determining the extent of internal H bonding with varying the dihedral angle θ . Parallel ab initio calculations are carried out in order to extend the experimental conclusions.

Experimental Section

The equilibrium proton-transfer reactions were studied in an ICR spectrometer built at the EPF—Lausanne and operated in the trapped-ion mode.⁶ The equilibrium process can be represented as in reaction 1 in which B stands for a reference base and AA for the amino alcohol.



Determination of the concentrations of the neutrals AA and B and of the ions BH⁺ and AAH⁺ at equilibrium yields the equilibrium constant K_{eq} for reaction 1. From the relationship $\Delta G = -RT \ln K_{\text{eq}}$, the change in free energy $\Delta G_r(1)$ can be obtained, giving the difference in gas-phase basicities, GB(AA) – GB(B). Estimation of the entropy changes in reaction 1 finally leads to the determination of the difference in proton affinities, PA(AA) – PA(B).⁷

An example of a time plot over a 1-s reaction time is reported in Figure 1. It can be seen that after having reached equilibrium, there is a slight but steady decrease in intensities of the signals due to ion loss from the trap.⁸ In order to determine the actual relative ion intensities due to the reactive processes, reaction 1, the experimental curves were fitted by a Monte Carlo method which is described in the Appendix. The resulting intensity values were divided by the ion mass in order to yield relative ion concentrations (first-order mass corrections⁹). For each couple of compounds studied, at least three separate measurements were performed with varying pressures of the neutrals. The reference bases were introduced via the dual inlet system of the ICR instrument. The temperature of the latter and of the vacuum can was kept constant at 50 °C. The amino alcohols studied are all solids at room temperature. They were introduced via a specially made inlet system which is directly attached to the vacuum can. The temperature around the probe was adjusted between 40 and 80 °C in order to maintain a constant pressure of the amino alcohol. Typical pressure conditions were the following: total pressure in the range of 2×10^{-6} to 4×10^{-6} torr with pressure ratio of the neutrals ranging from 0.3 to 4. The pressure readings are from an ionization gauge connected to the vacuum can. In order to translate these readings into concentrations, we used the values for the relative

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Table I. Free Energy Changes in the Proton Equilibrium Transfer Reaction $\text{BH}^+ + \text{AA} \rightleftharpoons \text{AAH}^+ + \text{B}$

AA ^a	B ^b	GB(B) ^c	ΔG_r	GB(AA) ^d
1	4-MPY	215.9	0.2	216.1 ± 0.2
2	4-MPY	215.9	0.3	216.2 ± 0.2
3	3-MPY	215.0	0.7	214.3 ± 0.2
4	3-MPY	215.0	-1.3	213.7 ± 0.3
5	CY	212.9	-0.1	212.8 ± 0.2
6	CY	212.9	-0.9	212.0 ± 0.4
	PY	212.6	-0.9	211.7 ± 0.3
7	CY	212.9	-0.9	212.0 ± 0.3
	PY	212.6	-0.5	212.1 ± 0.3
	SBU	212.1	-0.2	211.9 ± 0.3

^a AA = amino alcohol. ^b B = reference base (3- and 4-MPY = 3- and 4-methylpyridine, respectively, CY = cyclohexylamine, PY = pyridine, SBU = 2 butylamine). The relative cross sections of the neutrals are taken as follows: 1 and 5, 54; 2, 3, 4, and 6, 64; 7, 75; CY, 41; 3-MPY and 4-MPY, 37; PY, 30; SBU, 32. These values are estimated by the group equivalent method developed by Otvos and Stevenson (*J. Am. Chem. Soc.*, **78**, 546 (1956)). ^c Values in kcal/mol, taken from ref 1. ^d kcal/mol, error limits see the Appendix.

Table II. Gas-Phase Basicity and Proton Affinity Data for Amino Alcohols 1-7

AA	θ , deg	GB(AA) ^a	PA(AA) ^a
1	0	216.1	226.2 ^b
2	30	216.2	226.3 ^b
3	60	214.3	224.0 ^c
4	90	213.7	222.7 ^c
5	120	212.8	221.4 ^c
6	150	211.9	219.7
7	180	212.0	219.8

^a kcal/mol. ^b Entropy corrections assuming $\Delta S_{\text{cycl}} = -7.2$ eu. ^c Interpolated entropy corrections, see text.

ionization cross-sections, σ_{ioniz} , as reported in Table I.

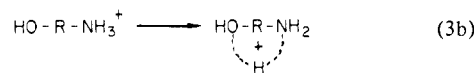
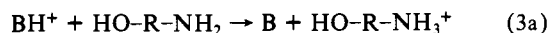
The synthesis of the amino alcohols has been already described.¹⁰ The reference bases were taken from commercial sources (Fluka). Gas-phase basicity and proton affinity data are all referred to the values for ammonia,¹ GB(NH₃) = 196.4 kcal/mol and PA(NH₃) = 205.0 kcal/mol.

Results

Table I summarizes the results obtained for the different pairs of compounds, and Table II summarizes the GB and PA data for the amino alcohols. Whereas free energy changes are readily obtained from the experimentally determined equilibrium constants, the determination of proton affinities requires the evaluation of the change in the entropy terms associated with the proton-transfer reaction. This implies that the structure of the protonated form be known. We have made the assumption that compound **7** in which $\theta = 180^\circ$ protonates in a reaction localized on the amino group (vide infra). In that case, the ΔS term for reaction 1 is due to symmetry changes given by the relationship 2. This term

$$\Delta S_r(1) = \ln \frac{\sigma_{\text{AAH}^+} \sigma_{\text{B}}}{\sigma_{\text{AH}} \sigma_{\text{BH}^+}} \quad (2)$$

is usually small as long as protonation occurs in a localized process.¹ The other assumption is related to the increase in basicity with decreasing value of the dihedral interfunctional angle θ . We assume that protonation of compound **1**, $\theta = 0^\circ$, is accompanied by formation of an internal H bond between the amino and hydroxyl groups. The overall protonation reaction can be conveniently decomposed in two steps, reaction 3. The entropy loss due



to the cyclization process is the predominant entropy terms, and

(10) References 6–10 cited in ref 3.

Table III. Computational Results on 2-Aminoethanol and 1,2-Ethanediol

compd	θ , deg	E_{tot}^a	δE^b	PA ^c	$d_{\text{N-O}}^e$	$d_{\text{N-H}}^e$	$d_{\text{O-H}}^e$
		-206.439 391 8					
		-206.441 78					
	180	-206.867 79	15.5	268.7 (230.7 ^d)	3.7516	1.0414	3.9243
	150	-206.866 44	16.3		3.6937	1.0413	3.8389
	120	-206.870 14	14.0		3.4980	1.0420	3.4570
	90	-206.874 82	11.1		3.1932	1.0427	2.9571
	60	-206.881 57	6.9		2.7297	1.0457	2.2082
	30	-206.892 08	0.25		2.3077	1.1299	1.3440
	19.2	-206.892 49	0	287.5 (237.4 ^d)	2.2976	1.1387	1.3142
	0	-206.892 115	0.24		2.2966	1.1453	1.2980
		-206.825 72		242.4 (199.6 ^d)			
		-225.955 82					
		-225.958 23		240.4 (196.1 ^d)			
	180	-226.341 405	28.2		$d_{\text{O-O}'}^e$ 3.6928	$d_{\text{O-H}}^e$ 0.9875	$d_{\text{O}'-H}^e$ 3.9314
	14	-226.386 356		270.1 (206.3 ^d)	2.20096	1.1665	1.1663

^a Hartrees. ^b $\delta E = E_{\text{tot}}(\theta) - E_{\text{tot}}(\theta = 19.2^\circ)$, kcal/mol. ^c PA = $E_{\text{tot}}(\text{M}) - E_{\text{tot}}(\text{MH}^+)$, kcal/mol. ^d PA with 4-31G basis set. ^e Calculated bond lengths, Å.

Table IV. Computational Results on 1,2-Ethanediamine

compd	θ , deg	E_{tot}^a	δE^b	PA ^c	$d_{\text{N-N}}^e$	$d_{\text{N-H}}^e$	$d_{\text{N}'-H}^e$
		-186.91950					
		-186.92405					
	180	-187.35757	21.9	272.0 (241.8 ^d)	3.8123	1.0415	4.1287
	150	-187.35641	22.6		3.7550	1.0416	3.8950
	120	-187.35270	24.9		3.5910	1.0414	3.5482
	90	-187.36158	19.4		3.2420	1.0432	2.9640
	60	-187.37341	11.9		2.6420	1.0633	1.9199
	30	-187.39220	0.16		2.3627	1.2513	1.2519
	17.8	-187.39245	0	296.8 (249.5 ^d)	2.3613	1.2486	1.2487
	0	-187.392296	0.10		2.3611	1.2464	1.2464

^a Hartrees. ^b $\delta E = E_{\text{tot}}(\theta) - E_{\text{tot}}(\theta = 17.8^\circ)$, kcal/mol. ^c PA = $E_{\text{tot}}(\text{M}) - E_{\text{tot}}(\text{MH}^+)$, kcal/mol. ^d PA with 4-31G basis set. ^e Calculated bond lengths, Å.

we may consider $\Delta S_r(1) = \Delta S_r(3b)$. One way for estimating this negative entropy term is provided by the thermochemical data for alkane \rightleftharpoons cycloalkane equilibria for which the respective values for ΔS° of -7.8, -10.7, -13.4, and -21.5 eu have been compiled for cyclopropane \rightleftharpoons *n*-propane, butane, pentane, and hexane equilibria.¹¹ On the other hand, Mautner et al.⁵ have reported experimental values of -8.0, -14.7, and -17.1 eu for the entropy of cyclization of protonated α,ω -diaminoethane, -propane, and -butane, respectively. It seems that the thermochemical values associated with the cyclization process compare best with the values for cycloalkane rings one member smaller.⁵ Therefore, for system 1 ($\theta = 0^\circ$), we have considered the thermodynamic data for the hypothetical butane \rightleftharpoons cyclobutane equilibrium ($\Delta S^\circ = -10.7$ eu). Taking into account that there is one internal rotation lost on protonation of 1, we have taken $\Delta S_r(1)$ as -7.2 eu for the systems 1 and 2. For compounds 3-5, the values for $\Delta S_r(1)$ were estimated by a linear interpolation between the values for $\theta = 0^\circ$ and $\theta = 180^\circ$. These arbitrary corrections will be discussed in the next section. The resulting proton affinities are given in the last column of Table II.

In deriving the PA data, we did not take into account the possibility for compounds 1-4 to chelate.¹² On the one hand this

would increase the differences Δ PA in proton affinity between compounds 1-4 and 5-7 by the corresponding energies for H bonding in the neutrals, and on the other hand entropy corrections $\Delta S_r(3b)$ would be cancelled.

In order to extend the experimental conclusions, we made molecular orbital calculations on the protonation of amino alcohols, diamines, and diols as a means of comparison with other experimental data.^{1,5,13} In a first approach we used the standard semiempirical methods MINDO/3¹⁴ and MNDO.¹⁵ These methods could be used only to evaluate the relative stabilities of O-protonated vs. N-protonated amino alcohols. In order to investigate the effect of conformation, we used an ab initio method which has been shown to be suitable for this kind of calculation.¹⁶ The ab initio calculations were made on a CYBER 170-270 computer using the MONSTERGAUSS program.¹⁷ The effect of

(12) Chelation of 1-4 has been observed in solution; for pertinent reference see M. Tichý, L. Kniežo, and S. Vašíčková, *Collect. Czech. Chem. Commun.*, **39**, 555 (1974).

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conformation on proton affinity was tested on two bifunctional compounds, i.e., 2-aminoethanol and 1,2-diaminoethane. The geometry of all calculated structures are fully optimized with the STO-3G basis set by the Davidson's method,¹⁸ the only geometrical constraint being the dihedral angle θ . The computational results are summarized in Tables III and IV. (All ab initio data are available as supplementary material.)

Discussion

Site of Protonation. The data of Table I show that there is a continuous increase in basicity (GB) with decreasing values for the dihedral angle θ . In view of the known alkyl substituent effects on basicity,¹ we can estimate that the slight variations in substituents in the amino alcohols 1-7 could change the intrinsic basicity by ± 0.2 kcal/mol at most. Therefore we can conclude that the changes in basicity with varying θ (Table I) are essentially of structural origin. The least basic member of the series, compound 7 in which $\theta = 180^\circ$, represents also the least favorable conformation for internal solvation in the protonated form. For the purpose of assigning the site of protonation under the present equilibrium conditions, we shall compare GB(7) with the basicity of monofunctional reference compounds. The following values are found:¹ GB(cyclohexylamine) = 212.9 kcal/mol and GB(cyclohexanol) = 187 kcal/mol. The latter value is estimated from the values compiled for analogous amino and hydroxy aliphatic compounds.¹ The present value of GB(7) = 212.0 kcal/mol clearly matches closely the value for cyclohexylamine. We conclude that protonation of 7 occurs to form a substituted ammonium ion $R-NH_3^+$.

This conclusion is supported by the results of the calculations (Table III): the difference in stability between the N- and O-protonated forms amounts to 28.4, 16.0, and 26.4 kcal/mol using the MINDO/3, MNDO, and ab initio methods, respectively (31.1 kcal/mol for the latter method with the 4-31G basis set). The ab initio result (26.4 kcal/mol) compares well with the difference in basicity for the two monofunctional compounds, i.e., GB(cyclohexylamine) - GB(cyclohexanol) = 25.9 kcal/mol. We can notice that the ab initio calculated proton affinity for the amino (267.3 kcal/mol) and the hydroxyl groups (240.9 kcal/mol) in the trans conformation of 2-aminoethanol is closely related to the calculated values for methylamine (263.5¹⁹ or 265.2 kcal/mol²⁰) and methanol (235.8 kcal/mol²¹). Consequently, protonation in *trans*-2-aminoethanol is localized on the amino substituent and there is no internal interaction between the two substituents in the protonated species. The calculated geometry is in agreement with this conclusion.

Similarly, protonation of both *anti*-1,2-diaminoethane and *anti*-1,2-dihydroxyethane is a localized reaction on one of the two amino and hydroxylic groups, respectively.

Intramolecular H Bonding. The observed increase in basicity of amino alcohols with θ decreasing from 180° to 0° is interpreted as the change in internal H bonding in the protonated amino alcohol. Our results indicate that in $1-H^+$, stabilization due to internal H bonding ranges from at least 4.1 and possibly up to 6.4 kcal/mol. These values correspond to the differences in GB and PA, respectively, between compounds 1 and 7 (Table II). Ab initio calculations on protonated 2-aminoethanol were carried out as a function of the dihedral angle θ (Table III). The results indicate that the most stable form occurs for $\theta = 19.2^\circ$ with a stabilization energy of 15.5 kcal/mol with respect to the anti-periplanar conformation. The geometrical parameters associated with the structure of minimum energy, in which the geometry was fully minimized without constraint, indicate that the stable species (by the STO-3G basis set) are *bridged* ions. Thus our calculations support the conclusion that the increase in proton affinity in the

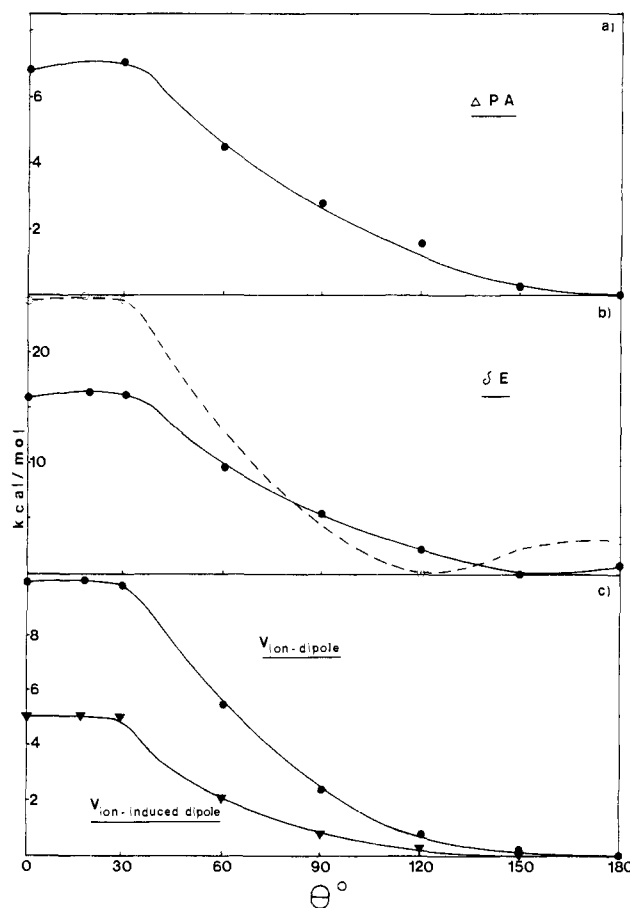


Figure 2. Dependence upon the dihedral angle θ : (a) difference in proton affinities, $\Delta PA = PA(X) - PA(7)$, (X) = (1)-(6); (b) difference in calculated stabilities δE for 2-aminoethanol and 1,2-diaminoethane (dashed curve); (c) ion-dipole and ion-induced dipole potential energy curves; both curves adjusted with reference to $7-H^+$ as zero energy.

series of amino alcohols 7-1 is due to internal H bonding.

It is of interest to visualize the change in proton affinity along the amino alcohol series. Figure 2a reproduces the experimentally determined values for $PA(X) - PA(7)$ as a function of dihedral angle θ , where X stands for compounds 1-6. It can be seen that there is no significant change when θ is varied from 0° to 30° (and from 180° to 150°). This is in accordance with the results of the calculated geometry for the most stable form in which $\theta = 19.2^\circ$. An approximately linear change is observed with θ varying from 30° to 150° . The results of the calculated differences in stability (δE) of protonated 2-aminoethanol are displayed in Figure 2b. A qualitative agreement is observed. It should be noted that the absolute values of calculated proton affinities are too high with the STO-3G basis set. This effect has been observed in the case of hydrogen bonds,²² in the case of ionic binding to monovalent cations,²³ and in the solvation of ions by water and ammonia.²⁴ In an attempt to obtain more reliable results, we have recalculated the STO-3G geometry with the 4-31G basis set (see last column of Tables III and IV). Although the absolute value of proton affinity and the difference $PA(\theta = 0^\circ) - PA(\theta = 180^\circ)$ decrease, the conclusion remains independent of the basis set: the formation of an internal H bond in protonated bifunctional bases is responsible for the increase in proton affinity.

Calculations performed on 1,2-diamino- and -dihydroxyethane lead to the same conclusion: the most stable form occurs for values of $\theta = 17.8^\circ$ and 14° , respectively (see Tables III and IV). In these cases the geometrical parameters indicate that the stable species are *symmetrically bridged* ions. The calculated δE values

(17) We thank Prof. I. G. Csizmadia and Dr. M. Peterson, University of Toronto, for a copy of this program.

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Table V. Summary of Calculated and Experimental Values^a

	calculated			experimental			
	bond length, Å	θ , deg	δE^b	c	d	e	f
Intramolecular Solvation							
N...H...N	1.249-1.249	17	22	6.7	14	18	
N...H...O	1.139-1.314	19	15.5	0	8.8	14	6.4
O...H...O	1.1665-1.1663	14.8	28			19	
Intermolecular Solvation							
N...H...N	1.087-1.644 ^g		27-31 ^g	23 ^h			
N...H...O				17 ^h			
O...H...O				32 ^h			

^a kcal/mol. ^b See Tables III and IV. ^{c-e} Bifunctional compounds, X(CH₂)_nY, with n = 2, 3, and 4, respectively, values taken from ref 1 and 5. ^f Table I. ^g Values from ref 16b. ^h Values from ref 13.

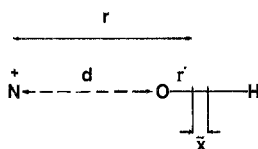


Figure 3. Geometrical parameters used for the determination of $V_{\text{ion-dipole}}$ (see text).

for 1,2-diaminoethane as a function of θ are also displayed in Figure 2b showing a similar dependence upon θ as already observed for 2-aminoethanol.

An interesting comparison can be made between the differences in stabilization energies (δE values) in the protonated forms of the three disubstituted ethane compounds studied (Table V): the largest stabilization energy is found in the symmetrical bifunctional species, dihydroxy compounds being stabilized to an upper extent than diamino compounds. This trend seems also to show up in the experimental data summarized in Table V for both the intra- and intermolecular solvation. This behavior is in accordance with recent observations that protonated mixed dimers $B_1HB_2^+$ are most stable when the basicities of B_1 and B_2 are equal.²⁵ It can also be seen in Table V that the δE values show the best agreement with the experimental stabilization energies determined for butane derivatives. Considering the scatter and the limited amount of experimental results (see ref 1, 5, and 13), it remains speculative to make a quantitative comparison of the data. However, it appears that the calculated stabilization energies are systematically higher than the experimental ones for both intra- and intermolecular solvation. In the present stage the results do not allow for more detailed conclusions (see also the results obtained with the 4-31G basis set), but the order of solvation effects is correctly reproduced whichever basis set is used for the computation.

The Nature of Ion Solvation. The qualitative and quantitative description of H bonding in protonated amino alcohols is attempted by using a simple model that considers the interaction between the ammonium ion and the dipole consisting of the OH group. The interaction potential energy is given by the relationship 4,²⁶

$$V_{\text{ion-dipole}} = -\frac{q\mu_D \cos \alpha}{r^2} \quad (4)$$

where q is the unit charge, μ_D the permanent dipole moment, α the angle between the dipole orientation and the line joining the charge and the center of the dipole, and r the distance between the charge and the center of the dipole. $V_{\text{ion-dipole}}$ was calculated for different values of θ by taking $\mu_D = 1.66$ D for the hydroxy group²⁷ and $\alpha = 0^\circ$. Values for $r = d + r'$ were estimated as follows (Figure 3). The values for d were taken from the N-O distances calculated by the ab initio procedure (see Table III).

(25) (a) W. R. Davidson, J. Sunner, and P. Kebarle, *J. Am. Chem. Soc.*, **101**, 1675 (1979). (b) See also ref 1, Table XV.

(26) See, for instance, C. H. Yoder, *J. Chem. Educ.*, **54**, 402 (1977).

(27) "Handbook for Chemistry and Physics", CRC Press: Cleveland, OH, 1978.

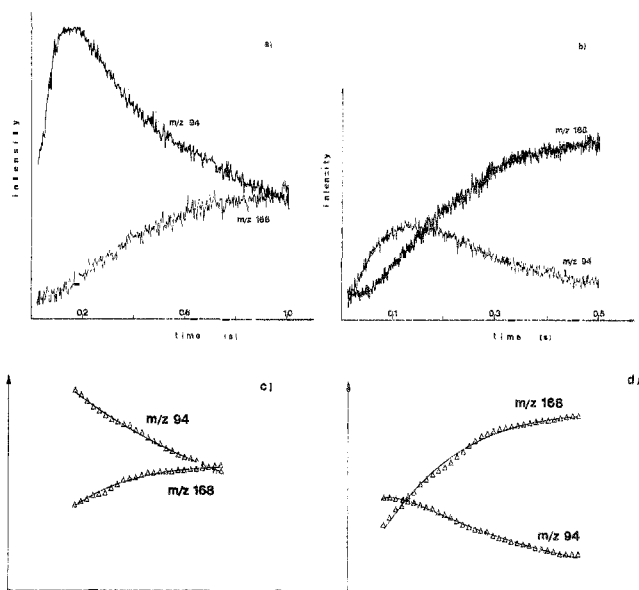
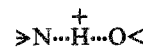


Figure 4. Time-dependent concentrations of the products of reaction 1 with AA = 2 and B = MPY with respective pressures of (a) 0.7×10^{-6} and 1.4×10^{-6} torr, (b) 1.5×10^{-6} and 1.7×10^{-6} torr. Parts c and d give the fitted curve (see the Appendix).

A constant increment r' was added to these values; r' represents the distance between the oxygen atom and the centroid of negative charge along the O-H bond. The dipole moment can be defined as $\mu_D = 2q\bar{x}$ where \bar{x} is the separation distance between the centroids of negative and positive charge. The latter lies at 0.48 Å from the oxygen atom (midpoint of the equilibrium O-H bond distance), thus yielding $\bar{x} = 0.17$ Å and $r' = 0.31$ Å. The resulting values for the charge-dipole potential energy are reported in Figure 2c for θ varying from 0° to 180° . The dependence of θ is seen to be similar to the dependence of ΔPA and δE given in Figure 2a,b. Moreover the difference values between $\theta = 0^\circ$ and $\theta = 180^\circ$ amounts to about 10 kcal/mol, suggesting that stabilization in protonated amino alcohols can be well reproduced by the model of charge-dipole interaction between the ammonium ion and the hydroxy group.²⁸ Possible contributions from charge-induced polarization forces cannot be overlooked, and they are also reported in Figure 2c: the potential energy $V_{\text{ion-induced dipole}} = -(\alpha_{\text{pol}}q^2)/2r^4$ was calculated by using an estimated value $\alpha_{\text{pol}} = 1$ Å³ for the polarizability of the hydroxy group.²⁹ The distance r was again taken as the N-O distance calculated by the ab initio procedure (Table IV). It can be seen in Figure 2c that the r^{-4} -dependent polarization interactions amount to about half the ion-dipole interactions at shorter distances ($\theta = 0^\circ, 30^\circ$) but rapidly decrease with increasing interfunctional distance. These data suggest that the stabilization observed in β -hydroxy ammonium ions is principally accounted for by the ion-dipole interactions between the ammonium ion and the hydroxy group.

A useful comparison between external and internal solvation of ions can be made on the basis of this model. We can assume that the proton-bound dimer systems yield values for H bond strengths which are essentially free from destabilizing effects. On the other hand, internal H bonding may cause significant changes in the geometry ultimately appearing as strain energy in the system. The strength of the unstrained



(28) It has to be noted that the ion-dipole interaction was calculated by using two assumptions: (1) the OH bond dipole is aligned with the line joining the charge and the center of the dipole ($\alpha \approx 0^\circ$) and (2) interaction of the C+→OH bond dipole is neglected since in that case the angle α has a value of about 100° .

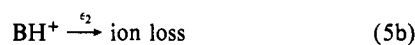
(29) The presently estimated value for $V_{\text{ion-induced dipole}}$ represents a higher limit; if a polarizable group larger than the OH group is considered, the concomitant increase in distance r tends to rapidly decrease the value for this potential energy term.

bond has been estimated as 17 kcal/mol.⁵ The difference between this value and the internal H bonding in 1-H⁺ can be represented as ΔH_{strain} in 1-H⁺ = 10.6 kcal/mol. As discussed by Mautner et al.,⁵ the weakening of the internal hydrogen bond may be due to several reasons such as the deformation of the σ -bond frame upon protonation and the effect of the charge on the electron distribution in the system (inductive-type effect). The series of amino alcohols presently studied should avoid some of these complicating effects that may contribute to ΔH_{strain} . In particular, there should be little, if any, deformation of the σ -bond frame upon protonation of 1 ($\theta = 0^\circ$) and 2 ($\theta = 30^\circ$) since the results of ab initio calculations (Table IV) predict that the most stable form of protonated 2-aminoethanol is characterized by $\theta = 19.2^\circ$. Nevertheless we find that systems 1-H⁺ and 2-H⁺ are stabilized by 6.5 kcal/mol only. The present work shows that the differences in stabilization energy between externally and internally solvated ions can be explained in terms of an ion-dipole interaction: whereas proton-bound dimers are able to reach the equilibrium geometry of the most stable conformation, the restricted approach of the ammonium ion and hydroxy group in 1-H⁺ and 2-H⁺ prevent efficient stabilization.

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Appendix

The evolution of the concentrations of ions as a function of time in the ICR spectrometer is essentially governed by two types of processes, i.e., reactive processes, reaction 1, and ion loss from the cell, reaction 5. We have neglected the possible formation



of dimers since they could be formed in processes with apparent second-order rate constants of approximately 10^{-12} cm³/(molecule-s) under the present experimental conditions (10^{-6} torr pressure range); see ref 30. Therefore these processes are unable to compete with the forward and backward processes of reaction 1 which occur with rate constants in the range of 5×10^{-10} cm³/(molecule-s).

The rate equations for the disappearance of ions are given by

$$d[\text{AAH}^+]/dt = \alpha[\text{BH}^+] - \beta[\text{AAH}^+]$$

$$d[\text{BH}^+]/dt = \gamma[\text{AAH}^+] - \delta[\text{BH}^+]$$

with

$$\alpha = k_1[\text{AA}] \quad \beta = (k_2[\text{B}] + \epsilon_1) \quad \gamma = k_2[\text{B}] \\ \delta = (k_1[\text{AA}] + \epsilon_2)$$

The solutions are

$$[\text{AAH}^+] = m_1 e^{r_1 t} + m_2 e^{r_2 t}$$

$$[\text{BH}^+] = n_1 e^{r_1 t} + n_2 e^{r_2 t}$$

with

$$r_{1,2} = \{-(\beta + \delta) \pm [(\beta - \delta)^2 + 4\alpha\gamma]^{1/2}\}/2$$

The solution can be written as

$$[\text{AAH}^+] = m_1 \left\{ 1 + \frac{m_2}{m_1} e^{-[(\beta - \delta)^2 + 4\alpha\gamma]^{1/2} t} \right\} \exp \left\{ -\frac{(\delta + \beta)}{2} + \frac{[(\beta - \delta)^2 + 4\alpha\gamma]^{1/2}}{2} \right\} t$$

If there is no loss, we have $\delta = \alpha$ and $\beta = \gamma$ so

$$[\text{AAH}^+] = m_1 \{ 1 + (m_2/m_1) e^{-(\alpha + \gamma)t} \}$$

We see that the second exponential term can be interpreted as a measure of the ion loss.

The fitting of the function with the general form given by

$$y = a_1(1 + a_3 e^{-|a_2|t}) e^{-|a_4|t}$$

was performed by using a Monte Carlo method for minimizing the sum of the absolute differences between the experimental curve and the fitted data. This criterion was used because it gives less weight to points which are way off the fitted curve than would a least-squares procedure. The program was written in FORTRAN IV language on a DEC PDP 11-34 computer.

It is important to point out that the treatment of the data according to the present procedure does not reduce significantly the error limits on ΔG values for systems in which the ion concentrations can be well estimated from the time-dependent ion intensities: such an example is provided in Figure 1. On the other hand, proton-transfer reactions may yield curves from which it is difficult to evaluate the ion concentrations at equilibrium. An example of this situation is given in Figure 4 where two runs of the same reaction system obtained in different conditions are shown. The experimental values for ΔG_r were 0.8 and 0.5 kcal/mol when calculated directly from the curves, parts a and b, respectively, of Figure 4. Respective values of 0.4 and 0.3 kcal/mol were calculated from the coefficients of the fitted data, parts c and d of Figure 4. Applying the fitting procedure to our experimental data has two main effects: first the scattering of the data is reduced and second the relative intensities of smaller mass ions is enhanced. Concerning the latter effect, it was generally observed that the coefficient a_4 which is a measure of the ion loss was inversely dependent upon ion mass. In other words, this corresponds to an increase in ion-trapping efficiency as the magnetic field is increased while keeping the frequency of the marginal oscillator constant.

Registry No. 1, 17997-65-8; 2, 52305-49-4; 3, 29910-43-8; 4, 33540-02-2; 5, 40335-14-6; 6, 33701-54-1; 7, 73495-63-3.

Supplementary Material Available: A listing of all the Cartesian coordinates of ab initio calculations on 2-aminoethanol, 1,2-ethanediamine, and their protonated forms (13 pages). Ordering information is given on any current masthead page.

(30) W. Davidson, M. T. Bowers, T. Su, and D. H. Aue, *Int. J. Mass Spectrom. Ion Phys.*, **24**, 83 (1977).