(4) Hydrogen-bond formation in open water-2-R-pyridine dimers leads to charge transfer from the substituted pyridine molecule to the water molecule, to characteristic changes in the electron densities of the O, H, and N_1 atoms which form the O–H···N_1 hydrogen bond, and to a redistribution of the π electron density of the pyridine ring.

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(28) The B dimers are described by the angular coordinates $\theta_1 = 50$, $\theta_2 = 180$, $\chi_1 = \phi = 0$, and $\chi_2 = 90°$. The O–N_1 distance is that found in the corresponding more stable A or C structure except for the water-2-aminopyridine dimer, where R is the distance in the A structure.
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(31) This dimer is further stabilized when the water molecule bends out of the dimer symmetry plane to direct one of the oxygen lone pairs toward the OH group.
(32) The data for the water-2-pyridinecarboxaldehyde dimer have been omitted, since the n orbital in 2-pyridinecarboxaldehyde is highly delocalized over the pyridine nitrogen and the carbonyl oxygen, and is not a suitable measure of the electronic environment at the nitrogen.
(33) Previous studies have shown that a correlation exists between the n orbital energies and the proton affinities of a series of bases, provided that the n orbitals are similar. For example, see ref 20 and R. H. Staley, J. E. Kleckner, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 2081 (1976).
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# Proton Affinities of Ethylidenimine and Vinylamine

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Abstract: The proton affinity of ethylidenimine has been determined by ion cyclotron resonance to be 213.2 ± 2 kcal/mol relative to the value for NH_3 of 203.6 kcal/mol. This value is combined with the known heat of formation of the protonated species to give a value of 2 ± 4 kcal/mol for the heat of formation (298 K) of the neutral imine. The proton affinity for C-protonation of vinylamine was calculated using ab initio molecular orbital theory with a DZ + D basis set to be 7.0 kcal/mol higher than that of the imine, giving 220.2 kcal/mol. The proton affinity for N-protonation of vinylamine was calculated to be 18.7 kcal/mol lower than that for C-protonation. The calculated proton affinities for ammonia, methylamine, dimethylamine, and trimethylamine using the same basis set are also given.

The determination of molecular proton affinities can yield valuable insight into both solution and gas-phase properties.[1] Work to date has concentrated on common functional groups, in particular, the proton affinities of amines.[2] We have begun to look at the gas-phase ion chemistry of some more unusual functional groups, including enamines and imines, and report here some initial ion cyclotron resonance (ICR) studies and ab initio calculations in this area.

Enamines are a classic example of an ambident reagent showing reactivity at both C and N with electrophilic species. This property is illustrated below for the reaction of a proton with the simplest enamine, vinylamine (**1**). Interestingly
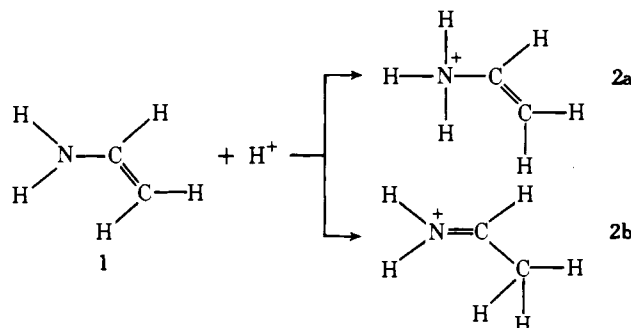
enough, in solution, for both protonation and the synthetically important alkylation reactions, the enammonium ion (e.g., **2a**)

Table I. Proton-Transfer Reactions Used in Determining the Proton Affinity of Ethylidenimine[a]

| base	double resonance[b] result	PA[c]
1. NH_3	no	203.6[d]
2. $(CH_3)_2SO$	no	210.8[e,f]
3. CH_3NH_2	no	212.7[g]
4. (CH₃-substituted aniline)	no	212.9[d]
5. (2-chloropyridine)	yes	213.4
6. (propyl-NH₂)	yes	215.1[g]
7. $(CH_3)_2NCOCH_3$	yes	215.3[f,h]
8. $i\text{-}PrNH_2$	yes	218.0
9. $PhCH_2NH_2$	yes	218.3[d]
10. $(CH_3)_3N$	yes	222.9[e]
11. $(CH_3CH_2)_2NH$	yes	223.7[i]
12. (imidazole N—CH₃)	yes	226.4[d,j]
13. (cyclic N—CH₃)	yes	227.4[i]

[a] All reactions were carried out with **2b**, **2b**-d_3 from **6**, and **2b**-d_2 from **7** unless otherwise indicated. Double-resonance results for a given base with each of the three isotopically different iminium ions were self-consistent. [b] A positive double resonance result means that **2b** is observed to transfer a proton to the respective base. [c] Proton affinity in kcal/mol. All PA values are based on the value for NH_3 from ref 11. All relative values except as noted are from ref 2. [d] **2b** only. [e] **2b**-d_3 only. [f] R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Eds., Chapman and Hall, London, 1975, Chapter 2. [g] **2b** and **2b**-d_3 only. [h] **2b** and **2b**-d_2 only. [i] **2b**-d_2 only. [j] J. L. Beauchamp, private communication.

is often formed in kinetic preference to the more stable immonium ion (e.g., **2b**).[3] Alternatively, **2b** may be reached by protonation of an isomer of **1**, ethylidenimine (**3**).
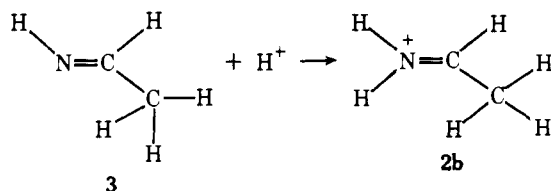
Neither **1** nor **3** is a stable species and consequently little is known about their chemical and physical properties. Yet from a theoretical point of view their simplicity makes them perhaps the most important representatives of each functional type. Existing information about these molecules comes from microwave studies of the product mixture of the flow pyrolysis of ethylamine,[4] inferences from more stable substituted analogues,[5] mass spectral studies,[6] and theoretical calculations.[7] Using an approach which combines both theory and experiment, we have generated thermochemical data on these short-lived neutrals and their conjugate acids. This approach is similar to that employed by other groups on other unstable systems.[8]

It is possible to generate the ion **2b** from electron bom-

$$+ \cdot CH_3 + 2e^-$$
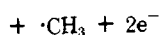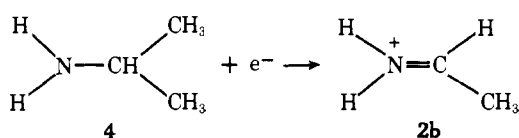
bardment fragmentation of isopropylamine (**4**) (through loss of a methyl group) in an ICR apparatus.[6,8] Proton-transfer reactions of the form $2b + B \rightarrow A + BH^+$ can then be studied. By varying the proton affinity (PA) of B, that of A may be inferred, assuming that all exothermic proton transfers can be observed, while endothermic processes cannot. This bracketing technique has been widely used for obtaining relative proton affinities in previous ICR investigations.[8b,9]

All experiments were carried out in the drift mode in the ICR apparatus and double resonance was used to identify and confirm reaction paths.[10] The proton-transfer reactions used to obtain the proton affinity of A relative to that of NH_3 are shown in Table I. These bracketing reactions establish that the proton affinity of A is 213.2 ± 2 kcal/mol based on the value of 203.6 kcal/mol recently reported for the proton affinity of NH_3.[11] We note that the absolute proton affinity of NH_3 is not established unequivocally, with values ranging from 202 to 208 kcal/mol.[12] Our reported value for the absolute proton affinity of A therefore is uncertain by a few kcal/mol. However, the value for the relative proton affinity should be more accurate, subject to the possible errors discussed below.

(1) Ions formed by electron impact ionization may contain substantial vibrational energy. If proton transfer does occur from these "hot" molecules, then the observed proton affinity would be lower than the actual value, i.e., the reaction establishing the upper bound might be suspect. In order to test for the contribution of "hot" molecules to proton transfer under these conditions, several experiments were carried out in the presence of argon as bath gas. At argon partial pressures of 10:1 ($P_{total} \sim 1 \times 10^{-4}$ Torr), the threshold for proton transfer was unchanged, with transfer from **2b** to 2-chloropyridine (**5**, Table I) being observed for all Ar pressures, suggesting that **2b** is not reacting as a vibrationally excited ion.[8f,13a]

(2) Isopropylamine, which is present as the precursor to **2b**, is a stronger base than the bases which bracket the proton affinity of A. As a result, proton transfer from **2b** to isopropylamine competes with the less exothermic proton transfers used in the bracketing (entries 1–7, Table I). It is possible that the observed threshold might be determined by the kinetic competition between proton transfer to isopropylamine and the weaker reference base rather than the exo- or endothermicity of the transfer. Several observations, however, suggest that this is not the case. (a) The ion **2b** is always a dominant peak in the mass spectra of the systems studied. (b) Since, in general, proton transfer to amine bases is fast (10–100% of the collision rate), even near thermoneutrality, effective competition should be preserved.[13b] (c) The close bracketing, in which the threshold is defined by two bases that differ in proton affinity by only 0.5 kcal/mol, suggests that this is a thermochemical rather than kinetic threshold. (d) In a model system, we have observed proton transfer from $CH_3NH_3^+$ to *m*-toluidine in the presence of isopropylamine (see Table I). This system approximates the thermochemistry in the bracketing reaction of **2b**, with proton transfer from methylamine to *m*-toluidine being 0.2 kcal/mol exothermic and proton transfer to isopropylamine 5.3 kcal/mol exothermic.[2]

Determination of the proton affinity of A does not identify A as either **1** or **3**. However, appropriate isotopic substitution of the parent isopropylamine can yield such information. We have synthesized the deuterated isopropylamines **6** and **7**,
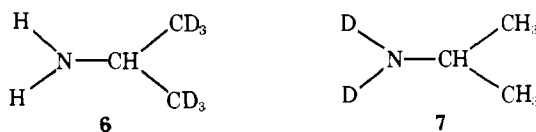
which fragment to form **2b** (D_3) from **6** and **2b** (D_2) from **7**; we have examined their proton (deuteron) transfer reactions as shown in Table I. These studies show that the predominant

Table II. Calculated Relative Proton Affinities[a]

molecule	$\Delta\Delta E(DZ + D)$[b]	$\Delta\Delta E(DZ)$[c]	$\Delta\Delta H$-(exptl)[d]
NH$_3$	0[e]	0[f]	0[g]
NH$_2$CH$_3$	−11.1[h]	−8.5	−9.0
NH(CH$_3$)$_2$	−17.8	−14.2	−15.6
N(CH$_3$)$_3$	−20.5	−17.2	−19.8
HNCHCH$_3$ (3)	−13.9		−9.6[b]
H$_2$NCHCH$_2$(C) (1)	−20.8		
H$_2$NCHCH$_2$(N) (1)	−2.1		

[a] All values in kcal/mol. [b] This work. [c] Reference 21. [d] Reference 2. [e] The calculated value at the DZ + D level for PA(NH$_3$) is 215.8 kcal/mol. The value at the DZP level is 217.7 kcal/mol. [f] The calculated value for PA(NH$_3$) = 221.9 kcal/mol. [g] PA(NH$_3$) = 203.6 kcal/mol. Reference 11. [h] The value for $\Delta\Delta E$ at the DZP level is 11.3 kcal/mol.

channels are transfer of H$^+$ from **2b** derived from **6** and transfer of D$^+$ from **2b** derived from **7**.[14] Based on this evidence, it seems clear that the proton affinity of A corresponds to that of ethylidenimine (**3**).

The only existing values for the proton affinities of imines are those of Aue and Bowers.[2] They report a value of −17.8 kcal/mol for the proton affinity of CH$_3$CH=NCH$_2$CH$_3$ relative to NH$_3$. Based on our result for the proton affinity of CH$_3$CH=NH this implies an ethyl/hydrogen substituent effect of 8.2 kcal/mol on nitrogen. In comparison, the value for this substituent effect in the corresponding saturated amines (sp^3 hybridization at N rather than sp^2 hybridization at N) diethylamine and ethylamine is 8.3 kcal/mol.[2] Wolf et al.[1] estimate that the proton affinity for methylenimine (CH$_2$=NH) is comparable to that of NH$_3$. Together with our proton affinity for **3**, this gives a methyl/hydrogen substituent effect at the unsaturated carbon atom in imines of ~10 kcal/mol. In conjunction with the heat of formation of **2b** measured from appearance potentials (156 ± 4 kcal/mol),[6] our value of the proton affinity leads to a heat of formation (298 K) of ethylidenimine of 2 ± 4 kcal/mol.

If one can obtain the energy difference between the two neutral isomers **1** and **3**, then this data also yields the proton affinity for C-protonation of vinylamine (**1**). Since this energy difference is not known experimentally, we have calculated it using ab initio molecular orbital theory (vide infra) to be $\Delta E(1-3) = 7$ kcal/mol with the imine being more stable. We thus predict a proton affinity of ~220 kcal/mol for C-protonation of vinylamine.

We have extended our study of the proton affinities of vinylamine and ethylidenimine using ab initio calculations. These calculations, even at the Hartree–Fock limit (see Table II), do not give accurate values for the absolute proton affinities owing to neglect of vibrational effects and of corrections from ΔE_0 to ΔH_{298} (correlation effects are presumably small[15]); thus, relative proton affinities must be examined. Previous workers have demonstrated that relative proton affinities can be obtained with reasonable accuracy from calculations employing at least a double ζ (DZ) basis set.[16] We have calculated the proton affinities for **1** and **3** relative to the calculated value for PA(NH$_3$). In order to calibrate our proton affinity scale we have also calculated the proton affinities of the methyl-substituted amines using the same basis sets. The theoretical proton affinities obtained in the manner described in the Experimental Section are shown in Table II relative to that of NH$_3$. The relative PA values are given quite well for the amines with our calculations showing slightly larger substituent effects than observed experimentally. We note that these calculated values for the relative proton affinities are the best available owing to the use of polarized basis sets and the use of optimized geometries for those not available experi-

mentally.[17] We have calculated the values for the proton affinities for protonation at both the C and N sites in vinylamine. Protonation at C is favored by 18.7 kcal/mol over protonation at N, which is in good agreement with previous double ζ calculations.[7c] Both of the larger basis set results show a substantial disagreement with the minimum basis set results of Müller and Brown.[7b] Using the above value for the PA for C-protonation leads to a predicted value of 202 kcal/mol for N-protonation of vinylamine. The proton affinity of the imine is calculated as −14 kcal/mol relative to PA(NH$_3$) compared to our experimental value of −9.6 ± 1 kcal/mol. The experimentally observed ordering PA(MeNH$_3$) < PA(imine) < PA(Me$_2$NH) is also obtained theoretically. We are pursuing both experimental and theoretical work on more highly substituted enamines toward the goal of understanding their important and unusual solution chemistry.

Experimental and Computational Details

The experimental studies were carried out on a Varian V-5900 ion cyclotron resonance spectrometer operated in the drift mode. All experiments were done using a rectangular cell at room temperature. Such instrumentation has previously been described in detail.[10,18] Electron energies were approximately 18 eV and phase-sensitive detection of the ions was accomplished by pulsing the electron beam. Total pressures as measured by an ion gauge were on the order of 1–3 × 10^{-5} Torr with relative pressures of isopropylamine to reference base being approximately 1:1. Pressure calibrations at pressures above 1 × 10^{-5} Torr were made using an MKS Baratron Type 90 capacitance manometer following standard procedures. Double resonance experiments were carried out by sweeping the frequency of a second oscillator.[19] The double resonance frequency was applied in the analyzer region.

All chemicals used in this study except for the deuterated isopropylamines were obtained from commercial sources and were used without further purification. They were degassed by several freeze-pump–thaw cycles. Mass spectra showed no significant impurities. The deuterated compound **6** was prepared by LiAlH$_4$ reduction of the oxime of acetone-d_6. Compound **7** was prepared by the exchange of isopropylamine in D$_2$O. Owing to the labile nature of the deuteriums on the nitrogen in **7**, the inlet system was exchanged using D$_2$O vapor overnight.

The SCF calculations were carried out on CDC 6400 and Cyber 74 computers. The ab initio calculations were done using the program[20] HONDO:76 while the approximate molecular orbital calculations used in the geometry optimizations were done with the program PRDDO.[21] The proton affinities reported in Table II were obtained from ab initio calculations at the DZ + D level,[22] i.e., a double ζ(DZ) basis set was employed for all atoms and polarization functions were placed on the heavy atoms.[23] Geometries for neutral NH$_3$, CH$_3$NH$_2$, (CH$_3$)$_2$NH, and (CH$_3$)$_3$N were taken from experiment.[24] All other geometries were optimized at the minimum basis set level using PRDDO.[25] The geometries for NH$_4$$^+$ and NH$_3$ were optimized at the DZ + D level giving $R(N^+-H) = 1.014$ Å and $R(N-H) = 1.003$ Å. In order to prevent problems from using N–H distances obtained at the minimum basis set level, all N$^+$–H distances were then corrected to the former value while the N–H distances for vinylamine and the imine were set at the latter value. The absolute proton affinity calculated using an optimized geometry instead of the experimental geometry for NH$_3$ differs at the minimum basis set level by less than 1 kcal/mol while at the extended basis set level this difference is reduced to less than 0.5 kcal/mol.

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(25) Geometry results will be published separately: R. A. Eades, D. Weil, C. H. Douglass, M. Ellenberger, W. Farneth, and D. A. Dixon, to be published.

Intramolecular Ring-to-Ring Proton Transfer in Gaseous (ω-Phenylalkyl)benzenium Ions

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Abstract: Gaseous (2-phenylethyl)benzenium and (3-phenylpropyl)benzenium ions **1** and **2** are generated easily by mass spectrometric loss of ·CO2H from the positive molecular ions of the corresponding 1-(ω-phenylalkyl)-1,4-dihydrobenzoic acids **4** and **5**. The major secondary fragmentation is loss of benzene from **1** and **2**. It is shown by deuterium labeling that **1** and **2** ions undergo repeated ring-to-ring proton transfer reactions, equilibrating all of the 11 "aromatic" hydrogen atoms within ~10^{-5} s without involving those from the aliphatic chain. A competition between the ring-to-ring (quasi-*inter*molecular) proton transfer and proton shifts within the ring ("ring walks") is discussed.

Introduction

Since arenium ions have been found to play a central role as intermediate in electrophilic aromatic substitution, their properties have been investigated intensively. In particular, the relative stabilities of isomeric arenium ions and their reactivity toward isomerization have been of considerable interest.[1-3] Contrary to proton addition complexes generated in strongly acidic media,[2] arenium ions formed in the gas phase[3] are not influenced by solvation effects, thus offering the possibility to study their intrinsic reactivity.

In this contribution we report on the intramolecular proton transfer occurring in gaseous (2-phenylethyl)- and (3-phenylpropyl)benzenium ions, **1** and **2**, respectively. The approach used to obtain **1** and **2** is generally applicable to generate gaseous arenium ions. The positive molecular ions of C-3-substituted cyclohexa-1,4-dienes (formed upon ionization by electron impact) readily lose one of the groups at the diallylic C-3 position, yielding the corresponding arenium ions. These primary ions are assumed to be formed, at least originally, as 3-substituted benzenium ions (Scheme I).
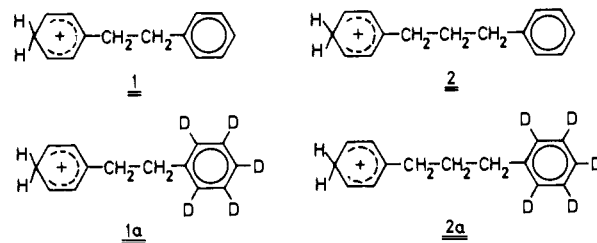
Results and Discussion

1 (*m/z* 183) and **2** (*m/z* 197) are generated by loss of CO2H from the molecular ions of 3-(2′-phenylethyl)-1,4-dihydrobenzoic acid (**4**) and 3-(3′-phenylpropyl)-1,4-dihydrobenzoic acid (**5**), respectively, as indicated in their 70-eV mass spectra (Figures 1a and 1c). In both cases this fragmentation is remarkably favored (apparent activation energies 5 and 7 kcal mol^{-1}, respectively[4]). Contrary to **4**$^{+·}$ and **5**$^{+·}$, their benzyl homologue **3**$^{+·}$[5] exhibits predominant cleavage of the *benzylic* C^3–C bond at 70 eV, thereby suppressing the loss of ·CO2H.[6]