proximating to those seen in the solid state. Since the boat-boat inversion barrier is evidently very low, such a distinction may not readily be resolved. This study has provided a unique opportunity for using crystallographic techniques to probe a molecular vibration in solution.

Acknowledgment. We are grateful to Professor M. J. Perkins (Chelsea College, University of London) for his help and advice.

Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters for carbon, hydrogen, and bromine, and final observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

Electronic Structure of Vinylamine. Proton Affinity and Conformational Analysis

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Abstract: Wave functions for vinylamine (**1**), ethylidenimine (**2**), and methylenimine (**3**) have been obtained at two levels of SCF theory, PRDDO and ab initio. All geometries were optimized at the level of PRDDO. A gradeint calculation with a DZD basis confirmed that the nitrogen is pyramidal in vinylamine. The ab initio calculations of the proton affinities of **1**, **2**, and **3** were performed with STO-3G, DZ, DZD, and DZP basis sets. The values for the PA's using the DZP basis relative to PA(NH_3) = 0.0 are -20.1, -14.9, and -4.6 kcal/mol for **1**-**3**, respectively. The energy difference with the DZP basis set between **1** and **2** is found to be 5.2 kcal/mol with **2** being more stable. The difference between C-protonation (iminium ion) and N-protonation (enammonium ion) of **1** is 18.3 kcal/mol favoring C-protonation. The rotation barrier about the C-N bond in vinylamine has been used to estimate a value of 6 kcal/mol for the strength of the conjugative interaction in **1**. The inversion barriers in the conjugated and nonconjugated forms of **1** were found to be low, 1.5 and 4.2 kcal/mol, respectively. Charge distributions show a significant delocalization of positive charge to the α carbon in the iminium ions. The ionization potentials determined from Koopmans' theorem are typical of those found in amines for **2** and **3**. The ionization potential for **1** is predicted to be quite low, 8.70 eV.

Introduction

Enamines $R_2C{=}CR'NR''_2$ are extremely important in a number of synthetic processes.[1] The reactions of enamines are strongly dependent on their electronic structure, particularly with regard to the nature of the conjugative interaction to the nitrogen. Although numerous substituted enamines have been synthesized, the simplest member of this group, vinylamine (**1**), is difficult to prepare and has not been studied in detail experimentally. Some experimental information about this molecule is available from flow tube studies in which its microwave spectrum was measured.[2] A detailed analysis of the microwave results has also been presented.[3] The proton affinity of vinylamine has been determined from a combination of theoretical calculations and measurements from ion cyclotron resonance spectroscopy.[4] However, most of our information about this simple compound has come from theoretical studies[5-8] which have been done either at the PRDDO level[5,9] or at the ab initio level with the STO-3G[10] and 4-31G basis sets.[11]

Ethylidenimine (**2**) is an isomer of vinylamine; the C-protonated form of vinylamine is identical with N-protonated form of the imine. Although this molecule also cannot be readily prepared and stored, its microwave spectrum[12] and matrix IR spectrum[7] have been obtained. Several theoretical studies of **2** have been published[13,14] and its proton affinity has been determined experimentally.[4] The simplest imine, methylenimine (**3**), is again not readily available for experimental studies,[15-17] and our knowledge of this model compound has come mostly from theory.[13,15,18-20]

Table I. Values for N-H Bond Distances for ab Initio Calculations[a]

basis	$r(\text{N-H})_{\text{pyr}}$[b]	$r(\text{N-H})_{\text{pl}}$[c]	$r(\text{N}^+\text{-H})$
PRDDO	1.033	1.008	1.040
DZ	0.995	0.989	1.012
DZD	1.003	0.991	1.014
DZP	1.001	0.989	1.012

[a] All distances in Å. From optimizations on NH_3 and NH_4^+ from ref 26. [b] Pyramidal nitrogen. These values are also employed in the imine calculations. [c] Planar nitrogen; ref 27.

As part of our program to obtain detailed information about the microscopic behavior of enamines and imines,[1] especially with

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Table II. Comparison of Geometry Parameters for CH_2NH

	method				
geometry parameter[a]	PRDDO[b]	DZD[b]	GTO-(73/3)[c]	STO-3G[d]	exptl[e]
r(CN)	1.262	1.257	1.257	1.273	1.273
r(NH)	1.048	1.009	1.018	1.048	1.021
r(CH)	1.085	1.083	1.081	1.091	1.09
r(CH')	1.082	1.081	1.075	1.089	1.09
θ(CNH)	111.9	113.8	114.1	108.1	110.4
θ(HCH)	114.6	115.5	115.7		117.0
θ(NCH_1)	125.8	125.4	125.2	125.4	125.1
θ(NCH_2)	119.6	119.1	119.1	119.1	117.9

[a] All bond distances in Å. All angles in degrees. [b] This work. [c] Reference 20. [d] Reference 13. [e] Reference 17.

regard to their gas-phase ion chemistry, we have studied the electronic structure of these three molecules using two levels of SCF theory. Calculations have been performed at the PRDDO level and at the ab initio level. At the ab initio level, we present a comparison (for some of the properties) of four basis sets: STO-3G, double ζ (DZ), double ζ plus heavy atom polarization (DZD), and double ζ plus polarization on all atoms (DZP). We have determined proton affinities for these compounds for use in our experimental studies. Calculations on vinylamine in a number of conformations, including rotamers and invertomers, have been carried out. The size of the rotation barrier about the C–N bond in vinylamine provides information about the maximum value for the conjugative interaction between the carbon–carbon double bond and the lone pair on nitrogen.

Calculations

The PRDDO calculations were carried out using the program as previously described.[9] The minimum basis STO exponents for C and N were taken from the work of Hehre, Stewart, and Pople[10] while the exponent on H was set at 1.2. The ab initio calculations were performed with the HONDO programs: versions 3 and 5.[22,23] The ab initio calculations of the proton affinities were done using DZ, DZD, and DZP basis sets. The conformational analysis at the ab initio level was only done using the DZP basis. The basis sets were taken from Dunning and Hay[24] and are based on the contraction scheme (9,5/4)/[3,2/2] at the DZ level.

Since complete geometries are not available from experiment, all geometries were obtained from geometry optimizations at the PRDDO level. The optimum geometry for vinylamine using the PRDDO method has been previously reported.[6] All other optimum geometries were obtained in this study. The molecule methylenimine and its protonated form are small enough so that geometry optimization with larger basis sets can be done in order to check the PRDDO results. Therefore, the optimum geometry for this molecule and the ion were also determined at the DZD level using a gradient scheme.[25] As discussed below, one gradient calculation for vinylamine was also carried out at the DZD level to check the adequacy of the PRDDO geometry.

As with most minimum basis sets, the N–H bonds obtained in the PRDDO optimizations are too long (see Table I). In order to provide geometries closer to the optimum geometry for each basis set beyond the minimum basis set, the following procedure was used to obtain scaled N–H distances. In a previous study of the proton affinities of methyl-substituted amines,[26] optimum geometries for NH_3 and NH_4^+ were obtained for each of the basis sets used in these calculations. These distances are shown in Table I. The N–H distance for the neutral compounds was set to the N–H distance found for NH_3 at that basis set level. For the protonated forms, the N–H distance from NH_4^+ appropriate to that basis set level was employed in the calculations. The PRDDO optimized geometries were used directly for the STO-3G calculations.

Table III. Comparison of PRDDO and DZD Geometries of CH_2CHNH_2

geometry parameter[a]	PRDDO	DZD	4-31G[b]
r(C_1N)	1.416	1.413	1.38
r(C_1C_2)	1.340	1.339	1.33
r(C_1H)	1.102	1.090	
r(C_2H)	1.091	1.085	
r(C_2H')	1.081	1.082	
r(NH)	1.024	1.003	
r(NH')	1.025	1.002	
θ($H'CH_2$)	115.8	115.8	
θ(HC_2C)	121.8	122.1	
θ($H'C_2C_1$)	122.4	122.1	
θ(HC_1C_2)	120.9	121.1	
θ(HC_1N)	113.3	113.4	114
θ(NC_1C_2)	125.7	125.4	126
θ(HNH')	109.4	109.4	
θ(HNC_1)	113.7	113.9	122
θ($H'NC_1$)	114.2	114.3	121
α	18.7	18.5	
β	145.2	145.3	
γ	164.7	164.8	
δ	38.2	38.0	

[a] All bond distances in Å. All angles in degrees. See Figure 1 for atomic labels and definitions of dihedral angles. [b] Reference 14.

Table IV. Comparison of PRDDO and DZD Optimized Geometries for $^+NH_2CH_2$

geometry parameter[a]	PRDDO	DZD	STO-3G[b]	4-31G[b]
r(CN)	1.281	1.272	1.29	1.26
r(CH)	1.096	1.077	1.11	1.11[c]
r(NH)	1.040	1.009	1.04	1.04[c]
θ(HCH)	118.2	118.8	118	118
θ(HNH)	114.2	117.1	116	115

[a] All bond distances in Å. All angles in degrees. [b] Reference 13. [c] Not optimized.

Results and Discussion

Geometries. In order to ensure that the PRDDO calculations were yielding good geometries, some geometry optimization was carried out at the DZD level for methylenimine, the protonated form of methylenimine, and vinylamine. The geometries at the PRDDO and DZD levels are compared in Tables II–IV together with results from other workers where appropriate. The DZD basis was chosen as a cost-effective compromise between a DZP basis and a DZ basis. This latter basis overestimates the stability of planar conformations at inverting nitrogens.[27]

The geometry for CH_2NH was optimized at the DZD level with the assumption of C_s symmetry, i.e., planarity. As shown in Table II, the optimum geometries from a variety of calculations are in good agreement with each other and with experiment.[17] The minimum basis sets show the largest errors for the value of r(N–H) and θ(C–N–H). The bond length for an N–H bond is typically found to be too long in comparison with such values from calculations using larger basis sets. The largest difference between the geometry determined with the largest basis (DZD) and experiment is for θ(CNH) which theory predicts to be somewhat larger. This is in accord with the shorter value for r(N–H) determined from theory.

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Table V. Summary of Heavy-Atom Bond Distances and Angles[a]

molecule	r(CN)	r(CC)	θ(NCC)
$NHCH_2$	1.262		
$^+NH_2CH_2$	1.281		
$NHCHCH_3$	1.265	1.492	122.5
$^+NH_2CHCH_3$	1.286	1.482	123.9
NH_2CHCH_2	1.416	1.340	125.7
NH_2CHCH_2 (pl 1)[b]	1.381	1.306	126.2
NH_2CHCH_2 (pl 2)[c]	1.399	1.297	124.1
$^+NH_3CHCH_2$	1.471	1.302	122.6

[a] All bond distances in Å. All angles in degrees. [b] See Figure 1g. Planar form. [c] See Figure 1h. Planar rotated form.

In examining the structure of formamide which is isoelectronic and isostructural with vinylamine, Radom[28] found that the STO-3G minimum basis set predicted a pyramidal nitrogen while the DZD basis predicted essentially a planar conformation at nitrogen. Because of the structural and electronic similarity between formamide and vinylamine, we carried out one gradient calculation on vinylamine at the DZD level. In contrast to Radom's work,[28] essentially no change in the geometry determined by PRDDO was found with the larger basis set. Both the nonplanarity of the ethylenic moiety and the angle of twist of the amino group about the CN axis are preserved. We are thus confident in the geometry determined at the PRDDO level.

The value of r(CN) and θ(CCN) for vinylamine have been determined from microwave spectroscopy[2] to be 1.397 Å and 125.2°, which are in excellent agreement with both the PRDDO and DZD values. Furthermore, the experimental results suggest but do not confirm a pyramidal nitrogen, a result supported by both the PRDDO and DZD calculations. In contrast to the above results, Houk et al.,[14] as shown in Table III, determined partially optimized geometries using a 4-31G basis (similar to a true DZ basis) and found a planar nitrogen. This planar conformation at nitrogen leads to a shortening of the CN bond, a typical phenomenon that is observed in comparing N–R distances at planar and pyramidal nitrogen.[27] The other parameters are in good agreement with our values. As has been shown previously, DZ basis sets always overestimate the stability of planar conformations at nitrogen and are thus inappropriate to use in this case. The DZD basis, in calculations on methyl-substituted amines,[27] has been shown to give good predictions of inversion barriers although the pyramidal conformation is slightly overstabilized; this basis does not overemphasize the stability of planar conformations at nitrogen.

As shown in Table IV, the geometries determined by various basis sets for $CH_2NH_2^+$ are in good agreement with each other. The exception, as mentioned above, is in the value of $r(N^+–H)$.

The PRDDO optimized geometries for the molecules and ions studied are shown in Figure 1 and important parameters are summarized in Table V. Very little change in the geometry of CH_2NH occurs on protonation except that the value for θ(CNH) increases by about 10°. The structure of the protonated imine **5** and of the N-protonated enamine **6** have also been determined by Jordan[8] at the STO-3G level. The PRDDO geometries are in reasonable agreement with the STO-3G results except that the bond distances between heavy atoms obtained from the PRDDO calculations are somewhat shorter. As expected from the methylenimine results, little change in geometry occurs in protonating **2** except that θ(CNH) increases. In contrast, N-protonation of vinylamine causes a significant change in the molecular structure of the neutral. The CN bond length shows a significant increase while the CC double bond length decreases. This would be expected because of loss of conjugation between the lone pair on N and the double bond by protonation on the lone pair.

Proton Affinities. The total energies of the ground-state structures are reported in Table VI as a function of basis set. The absolute proton affinities are given in Table VII, together with the proton affinity of NH_3 that we have previously determined.[26] The absolute proton affinities determined at the PRDDO level are large in comparison with those of larger basis sets, which is typical. The absolute values with the larger basis sets are, in turn, larger than experimental proton affinities. This is due predominantly to the neglect of zero-point differences between B and BH^+ in the theoretical determinations; inclusion of such effects will always lower the value of the absolute PA's.[29] Thus, for comparison with experiment, we report proton affinities relative to NH_3. These relative proton affinities are given in Table VIII. As expected, based on the results for the methyl-substituted amines,[26] relative PA's at the PRDDO level are given very poorly. The STO-3G basis provides much better relative PA's. Furthermore, the results with the larger basis sets are not in as good agreement with the experimental value for **2** as would have been expected based on our studies of methyl-substituted amines.[26] The largest basis set overestimates the value of PA(**2**) relative to PA(NH_3) by ~5 kcal/mol. The proton affinity of **1** is related to the proton affinity of **2** by the energy difference between the neutral forms of **1** and **2**. The proton affinity of **3** has been estimated to be comparable to that of NH_3;[30] i.e., the value for the relative PA(**3**) is 0.0. Experimentally this leads to a ΔPA between **2** and **3** of 9.6 kcal/mol with an error margin of ±2 kcal/mol. Our calculated difference for this value is 10.3 kcal/mol with the DZP basis, in very good agreement with the estimated experimental result. This result together with the DZD result suggests that the larger basis sets are properly describing the

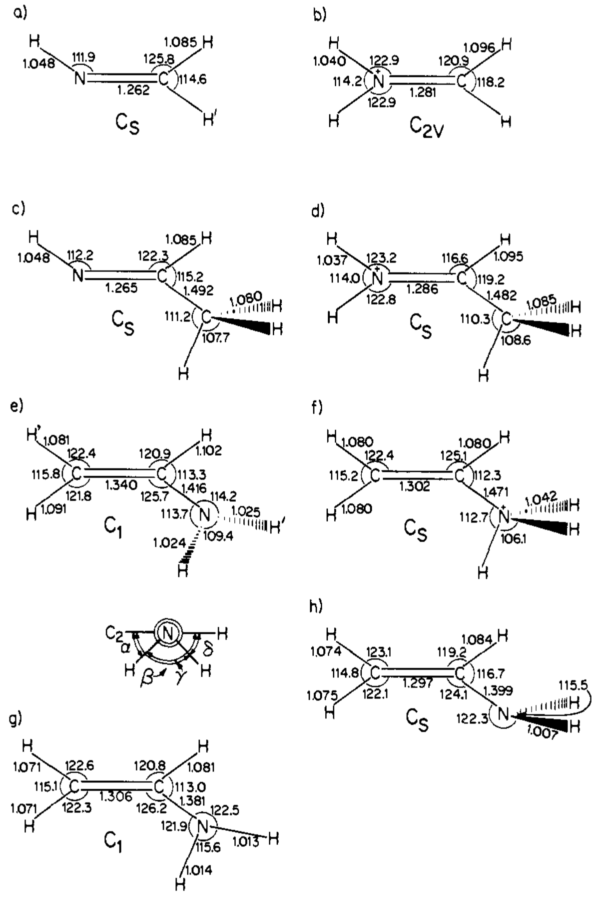

Figure 1. PRDDO optimized geometries. All parameters optimized unless noted: (a) $NHCH_2$, (b) $^+NH_2CH_2$, (c) $NHCHCH_3$ (scaled r(N–H) from $NHCH_2$), (d) $^+NH_2CHCH_3$, (e) NH_2CHCH_2 (geometry from ref 6; note the projection drawing showing labels for dihedral angles), (f) $^+NH_3CHCH_2$, (g) NH_2CHCH_3 (N-planar form), (h) NH_2CHCH_3 (N-planar form rotated about CN bond by 90°).

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Table VI. Total Energies of Neutral Molecules[a]

molecule	PRDDO	STO-3G	DZ	DZD	DZP
$NHCH_2$	-93.78518	-92.82252	-93.99430	-94.04492	-94.05228
$NHCHCH_3$	-132.79783	-131.41072	-133.02767	-133.09427	-133.10535
NH_2CHCH_2	-132.77673	-131.39358	-133.02909	-133.08318	-133.09705

[a] All energies in atomic units.

Table VII. Absolute Proton Affinities (in kcal/mol)

	method				
molecule	PRDDO	STO-3G	DZ	DZD	DZP
NH_3	259.1	260.3	221.1	215.8	217.7
CH_2NH	252.3	258.4	228.1	220.0	222.7
CH_3CHNH	263.5	270.1	237.7	229.7	232.6
CH_2CHNH_2 (N)	257.3	264.1	219.4	217.9	219.5
CH_2CHNH_2 (C)	276.8	280.9	236.8	236.6	237.8

Table VIII. Relative Proton Affinities (in kcal/mol)

	method					
molecule	PRDDO	STO-3G	DZ	DZD	DZP	exptl
NH_3	0.0	0.0	0.0	0.0	0.0	0.0
CH_2NH (3)	6.8	1.9	-7.0	-4.2	-4.6	
CH_3CHNH (2)	-4.4	-9.8	-16.6	-13.9	-14.9	-9.6[d]
CH_2CHNH_2 (N)[a] (1)	1.8	-3.8	1.7	-2.1	-1.8	
CH_2CHNH_2 (C)[b] (1)	-17.7	-20.6	-15.7	-20.8	-20.1	
Δ(C-N)[c]	19.5	16.8	17.4	18.7	18.3	
Δ*E*(**1**-2)	13.3	10.8	-0.9	6.9	5.2	

[a] N-Protonation. [b] C-Protonation. [c] Difference between C- and N-protonated forms. [d] Reference 4.

Table IX. STO-3G Vibrational Frequencies for NH_3, NH_4^+, CH_2NH, and $CH_2NH_2^+$ [a]

	NH_3	
mode	$\nu(NH_3)$	$\nu(NH_4^+)$
ν_1	3813 (A_1)	3774 (A_1)
ν_2	1408 (A_1)	1935 (E)
ν_3	4091 (E)	3987 (T_2)
ν_4	2077 (E)	1694 (T_2)

	CH_2NH	
mode	CH_2NH	$CH_2NH_2^+$
ν_1	1203	1017
ν_2	1218	1022
ν_3	1356	1167
ν_4	1602	1271
ν_5	1704	1450
ν_6	2006	1551
ν_7	3591	1750
ν_8	3756	1955
ν_9	3858	3584
ν_{10}		3743
ν_{11}		3908
ν_{12}		4085

[a] All frequencies in cm^{-1}.

Table X. Rotation and Inversion Barriers for Vinylamine[a]

method	1a-1b (rot.)	1a-1c (rot.)	1a(pyr)-1a(pl) (inv)	1b(pyr)-1b(pl) (inv)	1c(pyr)-1b(pl) (inv)
PRDDO	7.40	7.71	0.78	3.60	3.31
DZP	6.10	6.62	1.50	4.19	3.67

[a] All energies in kcal/mol: rot. = rotation barrier; inv = inversion barrier.

Table XI. Charge Distributions for Neutral and Protonated Species[a]

Charges for CH_2NH and $CH_2NH_2^+$

	method					
	PRDDO		DZP		STO-3G[b]	
atom/ group	CH_2NH	$CH_2NH_2^+$	CH_2NH	$CH_2NH_2^+$	CH_2NH	$CH_2NH_2^+$
C	0.03	0.22	-0.26	0.04	-0.08	0.12
CH_2	0.14	0.61	0.10	0.57	0.25	0.76
N	-0.29	-0.31	-0.40	-0.50	-0.55	-0.72
NH_n	-0.14	0.39	-0.10	0.43	-0.25	0.24

PRDDO Charges for 1, 2, P + 1 (1), and P + 1 (2)

atom/ group	H_2NCHCH_2	$H_3N^+CHCH_2$	$H_2N^+CHCH_3$	$HNCHCH_3$
C_α	0.08	0.05	0.30	0.10
$C_\alpha H$	0.12	0.15	0.47	0.14
$C_\beta H_n$	-0.06	0.18	0.19	0.03
N	-0.41	-0.37	-0.32	-0.31
NH_n	-0.06	0.66	0.34	-0.17

[a] All charges in units of electrons. [b] Reference 13.

methyl stabilization effect on iminium ions.

In order to determine if the errors in proton affinities relative to $PA(NH_3)$ are due to differences in relative zero-point energies, the values of ΔZPE in the harmonic approximation for NH_3 and CH_2NH were determined at the STO-3G level; these results are summarized in Table IX. Although the STO-3G basis may not yield extremely accurate force fields (the frequencies are ~15% high), relative trends in ΔZPE should be correct. (For example, ΔZPE for NH_3 is 10.3 kcal/mol determined from an extended basis set.[29]) The ΔZPE correction term reduces the absolute proton affinity for NH_3 by ~2 kcal/mol more than it reduces the absolute proton affinity for CH_2NH. Thus, inclusion of these approximate ΔZPE's would increase the disparity between calculated and experimental relative PA's for CH_2NH. It is thus likely that there is a significant correlation correction to PA(**3**). The direction of this effect would be to make CH_2NH more stable relative to $CH_2NH_2^+$ at the CI level.

The value for the absolute proton affinity for CH_2NH at the DZD level using the geometries optimized at this level is 220.7 kcal/mol which is in excellent agreement with the value obtained using the PRDDO optimized geometries and scaled NH bond distances. The value for the DZP basis using the DZD geometry with approximately scaled NH bond lengths is 223.4 kcal/mol which is again very similar to the value reported in Table VII. These results show that the choice of geometry introduces errors of <1 kcal/mol in absolute proton affinities. Relative proton affinities using values for $PA(NH_3)$ from optimized geometries at the DZD and DZP basis set levels were also calculated. The value determined in this way for $PA(CH_2NH)$ at the DZD level is -5.1 kcal/mol and at the DZP level is -5.9 kcal/mol. These values are again within 1 kcal/mol of the values reported in Table VIII using scaled PRDDO geometries and provide support for this method.

The relative proton affinities provide further information about basis set effects in these calculations. The STO-3G basis set yields proton affinities for CH_2NH and CH_3CHNH that are low compared to the values obtained using larger basis sets. The STO-3G PA's for these two compounds do agree well with experiment. The difference in energy between **1** and **2** is overestimated by the STO-3G basis by almost a factor of 2 (see Table VIII). The most interesting result is the ordering of the relative PA's for vinylamine and its isomeric imine at the DZ level. The DZ basis gives a larger PA to the imine, **2**, reversing the order of the larger basis sets and of the STO-3G basis. Thus the DZ basis predicts vinylamine to be *more* stable than the imine by ~1 kcal/mol contrary to the

Table XII. Ionization Potentials, Hydrogen Affinities, and Dipole Moments

molecule	IP[a](PRDDO)	IP(STO-3G)	IP(DZ)	IP(DZD)	IP(DZP)	HA[b](DZP)
$NHCH_2$	10.08	9.71	11.50	11.65	11.63	177.0
$NHCHCH_3$	9.77	9.38	11.19	11.35	11.31	179.6
NH_2CHCH_2 (1a)	7.38	6.92	8.73	8.70	8.70	124.6[c]
1b	8.88				9.85	
1c	8.98				9.92	
1a (N-planar)	6.99				8.34	
1b (N-planar)	8.46				10.11	

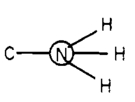
	dipole moments[d]		
	DZ	DZD	DZP
$NHCH_2$	2.61	2.31	2.29[e]
$NHCHCH_3$	2.62	2.33	2.32
NH_2CHCH_2	1.77	1.60	1.58

[a] Ionization potentials in eV. [b] Hydrogen affinity in kcal/mol. [c] Hydrogen affinity for C-protonated form. For N-protonated form, HA = 106.3 kcal/mol. [d] Dipole moments in Debye. [e] Value for DZP basis using optimum DZD geometry with scaled r(NH) is $\mu = 2.25$ D.

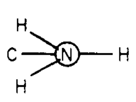
results of the larger basis set calculations and to most experimental evidence for more substituted systems.[31] The DZ basis, because of its preference for planar nitrogens, apparently overestimates the stability of vinylamine. The DZD basis slightly overestimates the energy difference between **1** and **2** in comparison with the DZP results.

The site of protonation in enamines is an important experimental question, and we examined both the C- and N-protonated forms of **1**. All of the calculations predict the C-protonated form (the iminium ion) to be more stable than the N-protonated form (the enammonium ion) by ~18 kcal/mol. This prediction of C-protonation over N-protonation is in agreement with the conclusions obtained in our gas-phase experiments on the site of protonation on simple substituted enamines.

Conformational Analysis of Vinylamine. There are a number of models that can be employed to estimate the strength of the conjugative interaction between the lone pair and the π bond. It is possible to estimate this quantity from a conformational analysis of vinylamine. If the NH_2 group is rotated such that the lone pair on nitrogen is perpendicular to the π bond, then no conjugative interaction exists. Thus the magnitude of the rotational barrier about the C–N bond provides a good estimate to the strength of this interaction. The geometries for the two rotamers were generated by the appropriate rotation about the CN bond in vinylamine. For the DZP calculations, scaling of the NH distances was done as described previously. The relative energies for the PRDDO and DZP calculations are given in Table X. Two conformations for the rotated NH_2 group exist:



1b



1c

Conformation **1b** is slightly lower in energy than conformation **1c** and is 6.1 kcal/mol higher in energy than the most stable conformation of vinylamine, **1a**. The slightly higher energy (6.6 kcal/mol relative to **1a**) for **1c** could be due to a small repulsive interaction between the lone pair on N and the two electrons in the N–H bond. It is unlikely that there is a significant steric interaction adding to the rotational barrier due to the geometric constraints of an sp^2 carbon atom and since no hydrogens are eclipsed. The energy difference between **1a** and **1b** can then be taken as the strength of the conjugative interaction which we estimate as 6 kcal/mol. This value, as expected, is somewhat lower than the value found for the allyl radical of 10–11 kcal/mol.[32] We note that the PRDDO calculations are in good agreement predicting a rotation barrier of 7.4 kcal/mol, 1.3 kcal/mol higher.

The inversion barrier at nitrogen in the conjugated form, **1a**, is quite low, being only 1.5 kcal/mol. This is significantly smaller than the corresponding inversion barrier in methylamine which has been computed to be 5.1 kcal/mol.[28] The decrease in the inversion barrier can be attributed to an increase in the overlap of the conjugating orbitals in the planar form. This leads to a decrease in energy of the planar form which opposes the increase in energy due to the inversion process at N. Perhaps a better comparison than the inversion barrier in methylamine is provided by the inversion barrier in the rotated form. This barrier is 4.2 kcal/mol based on the energy of the most stable rotamer. This barrier is slightly lower than that of methylamine, suggesting the presence of a small inductive effect due to the vinyl group. The difference in the two inversion barriers in vinylamine, 2.8 kcal/mol, represents the difference in the strength of the conjugative interaction between the pyramidal and N-planar forms of the most stable conformer of vinylamine. We note that the PRDDO inversion barriers are lower by ~1 kcal/mol. The DZP value for the inversion barrier is in reasonably good agreement with the value of 1.1 kcal/mol calculated by Meyer[3] from experimental microwave data.[2] Our somewhat higher value (by 0.4 kcal/mol) is in accord with our results for inversion barriers in methyl-substituted amines[27] where the calculated values for CH_3NH_2 and $(CH_3)_2NH$ are also slightly higher than the experimental values.

Charge Distribution. The Mulliken charge distributions[33] from the PRDDO calculations are shown in Table XI together with the DZP results for CH_2NH and $CH_2NH_2^+$. The atomic charges, as expected, considering the disparity in basis sets are somewhat different. However, the group charges, i.e., the charge for a CH_n or NH_n group, are remarkably similar between the two basis sets. The use of group charges helps to eliminate some of the ambiguities inherent in a Mulliken charge analysis and provides reasonable estimates of the locations of the charge. Considering the similarity between the group charges determined by the two methods for CH_2NH and $CH_2NH_2^+$, we feel that the PRDDO results do provide a semiquantitative estimate of the charge distribution in these molecules. The STO-3G results of Kollman (see Table 4) place too much positive charge on the CH_2 in comparison with the large basis set results. For $CH_2NH_2^+$, the group charges place more positive charge on the CH_2 group than on the NH_2 group. Substitution of a methyl group for hydrogen on C leads to a significant amount of positive charge delocalization on the methyl substituent. In fact, introduction of the methyl substituent removes charge from the NH_2 region and delocalizes it over the α-C and the α-CH_3 group. These charge distributions showing delocalization of charge to the α-C are in qualitative agreement with our experimental results on proton affinities which show a large methyl substituent effect at the α carbon. In the isomeric enammonium ion, the positive charge is highly localized on the nitrogen although some delocalization of this charge onto the vinyl group is observed (see Table XI).

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Ionization Potentials and Hydrogen Affinities. The ionization potentials (IP) determined from Koopmans' theorem[34] for the neutral species are reported in Table XII together with the dipole moments calculated with the larger basis sets. The ionization potential of CH_2NH is somewhat higher than that of CH_3NH_2 [10.48 eV (calculated[27]), 8.9 eV (experimental[35])]. Substitution of an α-methyl group to give **2** lowers the IP by 0.3 eV. The IP for vinylamine, in contrast to the imines, is much lower. For **1a**, the ionization potential decreases in the N-planar form as expected from results on methyl-substituted amines. This decrease in IP is significantly smaller for **1** than for the amines as expected from the small inversion barrier in **1**. Rotation about the CN bond which destroys the conjugation increases the ionization potential by 1.2 eV. In the planar form of **1b**, an increase in IP from that in pyramidal **1b** is actually predicted. This is contrary to the general observation that IP's decrease at planar nitrogens.

The hydrogen affinity (HA) defined by the reaction $MH^+ \rightarrow M^+ + H$ is related to the proton affinity (PA) as follows:

$$HA = PA + IP(B) - IP(H)$$

where IP is the appropriate ionization potential. The hydrogen affinities determined from our theoretical values are given in Table XII for the DZP results. These values are only approximate owing to errors in determining the IP from Koopmans' theorem and to errors in the absolute proton affinities; the qualitative trends, however, should be correct. The values for HA of the imines **2** and **3** are comparable showing a slight increase on methyl substitution. This is opposite to the effect of methyl substitution on HA's in amines. The hydrogen affinity for vinylamine is lower than that of its isomeric imine by ~50 kcal/mol. This is due primarily to the large difference in ionization potentials between the imine and the isomeric enamine.

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Proton Affinities and the Site of Protonation of Enamines in the Gas Phase

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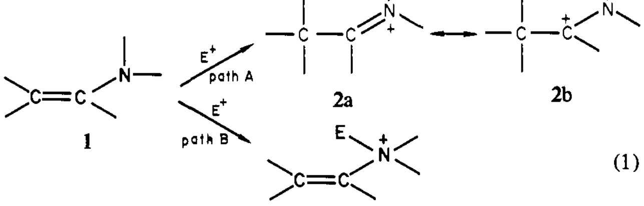
Abstract: The gas-phase proton affinities of a number of methyl-substituted enamines and imines have been measured using ion cyclotron resonance spectroscopy. Comparison of the effect of substituents on the proton affinities of the enamines with those of corresponding amines is used to show that protonation in the gas phase occurs at carbon leading to the formation of an iminium ion. The observation of a large substituent effect for substitution of an α-methyl group also suggests that there is a significant amount of delocalization of positive charge in the iminium ion. A comparison with solution-phase basicities of enamines is also presented.

Introduction

The enamine functional group is commonly employed in synthetic organic chemistry[1] and commonly encountered in biological chemistry.[2] It represents a classic example of an ambident reactant, showing nucleophilic reactivity at both the nitrogen and β-carbon atoms (reaction 1). In solution, the competition between C and N attack appears to be a very sensitive function of electrophile structure, enamine structure, and solvent.[3] In the particular case when E^+ is a proton, most mechanistic studies have shown preferential attack at N in some cases followed by rearrangement to the more stable C-protonated form.[4] In order to determine how intrinsic and solvation influences combine to direct reactivity in this interesting class of compounds, we have undertaken concurrent experimental and theoretical studies of the gas-phase ion chemistry of enamines.



(1)

We report here proton affinities of a number of differently substituted acyclic enamines as determined by ion cyclotron resonance (ICR) spectroscopy. In an accompanying paper extensive ab initio calculations on the simplest enamine and related imines are reported. A self-consistent picture of the gas-phase proton-transfer reactions of enamines and their isomeric imines is developed predicated on the following implications of the ICR data: (1) gas-phase protonation of enamines occurs exclusively at the β carbon atom to yield iminium ions (path A, Figure 1); (2) deprotonation of iminium ions having hydrogens at nitrogen

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[‡] Alfred P. Sloan Foundation Fellow (1977–1981), Camille and Henry Dreyfus Teacher Scholar (1978–1983), DuPont Young Faculty Grantee (1978).

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