141. Enamines I. Vinyl Amine, a Theoretical Study of its Structure, Electrostatic Potential, and Proton Affinity

by **Klaus Müller** and **Leo D. Brown**

Organisch-chemisches Laboratorium der Eidg. Technischen Hochschule Zürich,
Universitätsstr. 16, CH-8092 Zürich

(10.III.78)

Summary

The structure of vinyl amine and its reactivity towards a proton is studied by the PRDDO SCF MO method. The equilibrium structure is found to be non-planar and barriers to inversion- and rotation-dominated processes are calculated. Proton addition to vinyl amine, as a model of enamine protonation, is examined by means of electrostatic molecular potentials and *C- versus N*-proton affinities.

---

1. Introduction. - Enamines are readily accessible, highly reactive, and thus synthetically useful intermediates [1] [2]. They represent ambident conjugated systems with high nucleophilicity at both the nitrogen and the β-carbon atom [3]. Attempts to arrive at a detailed understanding of their chemical reactivity are faced with many intriguing problems. First, the relative site preference for electrophilic attack depends not only on the nature of the enamine but also on the electrophile and the solvent. Second, careful differentiation between kinetic and thermodynamic control is necessary but often quite difficult. Third, little is known about the structure of enamines, particularly the degree of intrinsic non-planarity of the enamine unit and its influence on nucleophilic reactivity. This last point is fundamental in discussions of the stereochemistry of electrophilic additions to enamines and is the subject of considerable experimental activity [4].

As a first step in a theoretical study of the structure and reactivity of enamines, the case of vinyl amine and its protonation is examined. Vinyl amine is prototypical of aliphatic enamines. Furthermore, it is of interest in view of recent semi-empirical calculations [5] [6] and a microwave spectroscopic analysis [7], which suggest this molecule to be non-planar [7] [8]. However, from the rather limited set of experimental data [7] no detailed structural information is available. Quantum chemical calculations on the structure and internal motions of vinyl amine thus provide a valuable basis for a more quantitative interpretation of its microwave spectrum [9].

2. Method. - All calculations were carried out using the approximate *ab initio* SCF MO method PRDDO (partial retention of diatomic differential overlap) [10]. *Slater* exponents were chosen for all atomic orbitals, excepting hydrogen

1s orbitals, for which exponents were set to 1.2. Geometries were optimized using the simplex method [11], approximate gradient procedures [12], or a combination of both.

3. Molecular structure of vinyl amine and barriers to internal motions. - Calculation of the energy hypersurface of vinyl amine **1** with respect to both pyramidal inversion at the nitrogen atom and torsion around the C–N bond[1]) resulted in a double-well potential *(Fig. 1)* with two symmetry-related non-planar equilibrium configurations and a planar transition state roughly 1.6 kcal/mol higher in energy.

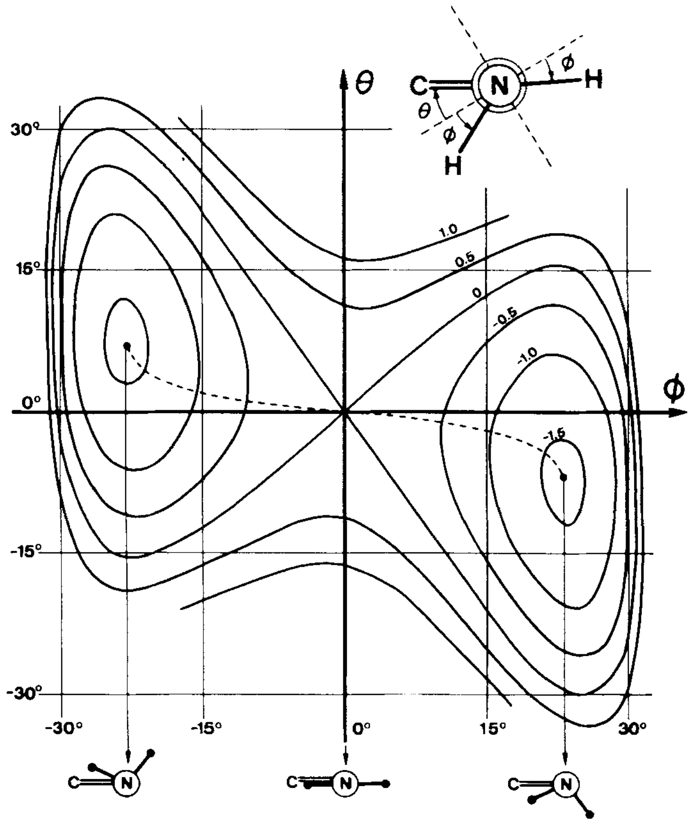


Figure 1. *Potential energy surface for pyramidal inversion at the nitrogen atom and internal rotation around the C–N bond in vinyl amine*[1]). The energies, in kcal/mol, are relative to the planar transition state.

---

[1]) The structural parameters used for **1** correspond to average values of those specified in *Table V* of [7]. Pyramidal inversion at the nitrogen atom and torsion around the C–N bond are described by the angles ϕ and θ, respectively, as defined in *Figure 1*. Bond angles at the nitrogen atom, γ, are assumed to be equal; they are related to ϕ by $\gamma = \arccos[(2\cos^2\phi)^{-1} - 1]$.

Complete geometry optimization of **1** produced structure **1a** *(Fig. 2)*, which confirmed the gross features of the equilibrium configurations as shown in *Figure 1*. Several structural aspects of **1a** are noteworthy. The configuration at the nitrogen atom is pyramidal, with average bond angles slightly larger than tetrahedral[2]. Pyramidalization at the nitrogen atom is coupled with a torsion around the C–N bond so that the N–H bond *syn* to the CC double bond moves less out of the CCN plane than the other N–H bond[3]. The vinyl group remains essentially planar, but is titled[4] so that the methine and the amino hydrogen atoms lie on opposite sides of the CCN plane. The methylidene and the amino group exhibit approximate C_{2v}- and C_s-symmetry, respectively[5].

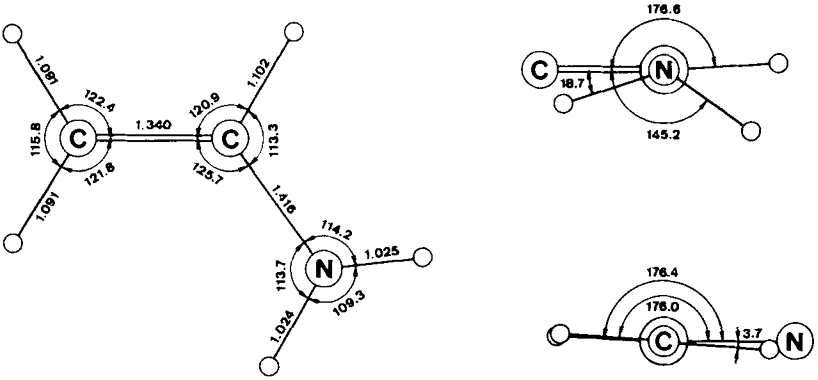


Figure 2. *Calculated geometry of the equilibrium configuration of vinyl amine* ($E_{SCF} = -83313.03$ *kcal/mol); molecular structure shown in projections onto the CCN plane and along the N–C and C=C bonds* (distances in Å, angles in degrees).

The nature of the transition state for the inversion-dominated process, as indicated in *Figure 1*, was verified by geometry optimization of **1** with only the constraint of a planar nitrogen configuration. This resulted in the all-planar structure **1b** *(Table 1)*. Transformation of **1a** to **1b** is accompanied by changes in bond distances, most notably a shortening of the N–C and N–H bonds by about 1 to 2 percent[6], whereas the CC double bond lengthens by only some 0.002 Å. Structure **1b** lies 2.4 kcal/mol above **1a**. Since PRDDO tends to over-

---

[2] Average bond angles of $\gamma \sim 112.4°$ correspond to $\phi \sim 26°$ in *Figure 1*.

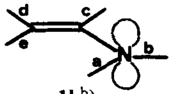
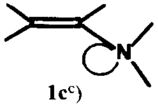
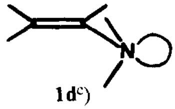
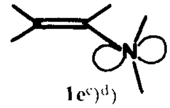
[3] From the two torsional angles τ(HNCC), θ, the amount of internal rotation around the C–N bound, is calculated to be $-8.1°$ *(Fig. 1)*.

[4] The angle between an average plane through the vinyl group and the CCN plane is about 3.8°.

[5] The semi-empirical calculations of [5] likewise produced a strongly pyramidal amino group, but no torsion around the C–N bond was found, and no tilting of the vinyl group was indicated. However, the same authors using the same method later reported [6] a somewhat different structure, which does display a torsion around the C–N bond, although it is rather small ($\theta = -1.5°$).

[6] Similar changes in bond distances are predicted by accurate *ab initio* SCF MO calculations to occur upon pyramidal inversion in ammonia [13] and in several simple amines [14].

Table 1. *Calculated energies and geometries*[a]) *for the non-equilibrium configurations* **1b**-**1e** *of vinyl amine*

	 **1b**[b])	 **1c**[c])	 **1d**[c])	 **1e**[c])[d])
E_{SCF}	−83,310.66	−83,305.92	−83,305.11	−83,298.16
r(CN)	1.391	1.453	1.453	1.424
r(CC)	1.342	1.339	1.338	1.339
r(NH) (a)	1.015	1.033	1.033	1.012
(b)	1.014			
r(CH) (c)	1.101	1.105	1.106	1.106
(d)	1.089	1.095	1.093	1.095
(e)	1.089	1.095	1.093	1.095
γ(CCN)	126.1	122.7	126.1	124.5
γ(HNH)	116.5	104.9	105.2	116.6
γ(CNH) (a)	121.4	110.0	110.1	121.7
(b)	122.1			
γ(CCH) (c)	120.8	119.3	119.8	118.5
(d)	122.2	122.5	122.8	122.6
(e)	122.1	121.8	122.1	122.1

[a]) Energies in kcal/mol; bond distances in Å; bond angles in degrees.
[b]) C_s-symmetry results from merely the constraint of a planar nitrogen configuration.
[c]) C_s-symmetry enforced.
[d]) Nitrogen configuration constrained to be planar.

estimate barriers to pyramidal inversion (see below), this value represents an upper limit for the experimental barrier.

Internal rotation around the C–N bond was examined by optimizing, under the constraint of C_s-symmetry, the geometries of conformations in which the CCN plane bisects the amino group. Structures **1c** and **1d**, which lie 7.1 and 7.9 kcal/mol above **1a**, respectively, were thereby obtained *(Table 1)*. Rigid rotation by small angles around the C–N bond confirmed them to be transition states for rotation-dominated processes. The torsional barriers in vinyl amine are thus considerably higher than the barriers to pyramidal inversion[7]). Among the structural changes which occur in going from the non-planar equilibrium configuration to either rotational transition state, are an increase in nitrogen pyramidality with a reduction of the average bond angles at the nitrogen atom by *ca.* 4° and a lengthening of the N–C and the N–H bond distances by about 3 and 1 percent, respectively. By contrast, the CC double bond distance remains virtually unchanged.

---

[7]) They are considerably smaller, however, than the energy difference of 12.5 kcal/mol between structures **1b** and **1e**, in which the nitrogen atom is forced to maintain a planar configuration.

Table 2. *Calculated and experimental geometries of small molecules related to vinyl amine*a)

$CH_2{=}CH_2$b)	CC 1.331 (1.336-1.339); CH 1.096 (1.085-1.103); CCH 122.6 (120.7-121.9)
$CH_3CH{=}CH_2$b)c)	C^1C^2 1.334 (1.336-1.342); C^2C^3 1.515 (1.501-1.506); C^1H^1 1.092 (1.091); C^1H^2 1.095 (1.081); C^2H^6 1.097 (1.090); C^3H^3 1.097 (1.085); $C^3H^{4,5}$ 1.099 (1.098); $C^1C^2C^3$ 125.1 (124.3); $C^2C^1H^1$ 122.4 (120.5); $C^2C^1H^2$ 122.7 (121.5); $C^1C^2H^6$ 119.3 (119.0); $C^2C^3H^3$ 111.5 (111.2); $H^3C^3H^{4,5}$ 107.8 (109.0); $H^4C^3H^5$ 106.8 (106.2); $H^3C^3C^2C^1$ 0 (0)
NH_3b)	NH 1.032 (1.012-1.030); HNH 105.0 (106.7-107.5)
CH_3NH_2b)d)	CN 1.470 (1.465-1.471); NH 1.028 (1.010); CH 1.106, 1.108e) (1.099); CNH 109.6 (110.3); HNH 105.1 (107.1); HCH 107.0, 107.8f) (108.0); δg) 2.9 (2.9)

a) Bond distances in Å rounded to three decimals; bond angles in degrees rounded to one decimal; experimental values in parentheses.

b) Ranges of experimental values according to [15].

c) Numbering scheme according to [15]; unique experimental values taken from [16].

d) Unique experimental values taken from [17].

e) The larger value refers to the unique CH bond.

f) The larger value refers to the angle between the two symmetrically related CH bonds.

g) Angle between the C—N bond and the axis through the carbon atom having equal angles to the CH bonds.

To place these results in perspective, the structures of small molecules related to vinyl amine were also examined. Comparison with experimental data shows that equilibrium geometries *(Table 2)* are rather well reproduced by the PRDDO method, bond distances falling within 0.01-0.02 Å of corresponding experimental values and bond angles deviating by not more than 1-3°. The structural predictions of PRDDO are thus similar in quality to those of standard *ab initio* SCF MO

Table 3. *Calculated and experimental barriers*a) *to internal motions in small molecules related to vinyl amine*

		Barriers to pyramidal nitrogen inversion	
		calculated	experimental
	NH_3	10.8	5.8 [19]
	CH_3NH_2	8.8	4.8 [20]
1	$CH_2{=}CHNH_2$	2.4	1.0-1.3 [8] [9]
		Barriers to internal rotation	
		calculated	experimental
	$CH_3\ni NH_2$	2.6	2.0 [17]
1	$CH_2{=}CH\ni NH_2$	7.1b); 7.9c)	-
	$CH_2{=}CH\ni CH_3$	1.4	2.0 [21]
3	$CH_2{=}CH\ni \overset{+}{N}H_3$	1.4	-
2	$CH_3\ni CH{=}\overset{+}{N}H_2$	1.1	-
	$CH_3\ni CH{=}O$	-	1.2 [22]

a) All quantities in kcal/mol rounded to one decimal.

b) Rotation through **1c**.

c) Rotation through **1d**.

methods using minimum basis sets [18]. *Table 3* compares calculated and experimental barriers to internal motions. As can be judged from the results for ammonia and methylamine, PRDDO tends to overestimate barriers to pyramidal inversion by roughly a factor of two. Accordingly, a barrier near 1.2 kcal/mol may be predicted for the inversion-dominated process in vinyl amine, in close agreement with values ranging from 1.0 to 1.3 kcal/mol as determined from the microwave spectroscopic data of **1** [8] [9]. Internal rotations around single bonds appear to be handled fairly well by PRDDO, which gives reasonable estimates for rotational barriers and correct predictions for conformational preferences. In *Table 3* the results for the two protonated species **2** and **3** are also included. In both cases the most stable conformation is found to be the one in which a single bond of the three-fold rotor eclipses the double bond, as is known to be the case in propene [16] and acetaldehyde [23]. Furthermore, torsion around the C–C bond in methyl immonium **2** is predicted to be less hindered than torsion around the C–N bond in vinyl ammonium **3**. This result shows an interesting parallel to a similar reduction in the experimental rotational barrier in going from propene to acetaldehyde.

The success of PRDDO in reproducing equilibrium geometries and trends in barriers to conformational and configurational changes gives confidence that the calculated non-planar equilibrium structure for vinyl amine as well as the description of inversion- and rotation-dominated processes is quite realistic. Our conclusion is supported by the fact that a model potential [9] based on these theoretical results is capable of reproducing all available microwave spectroscopic data for **1**.

4. Proton addition to vinyl amine as a model of enamine protonation. – Our study of the reactivity of vinyl amine towards a proton is based on the electrostatic potentials of **1a–1e** with respect to a positive point charge; on their vertical proton affinities, *i.e.*, protonation energies in the absence of geometric relaxation in the nucleophile; and on the proton affinities of **1**, as obtained from the energy differences between **1a** and the fully optimized structures of the C- and N-protonated species **2** and **3**, respectively.

Examination of electrostatic potentials allows us to judge long-range interactions between a proton and vinyl amine and to assess the relative site preference for proton attack by charge control [24]. Maps of equipotential curves for **1a** and **1b** through planes parallel to the CCN plane are shown in *Figure 3*.

Consider first the planar transition state **1b**. Four minima of almost equal energy, symmetrically related in pairs, can be located on its potential surface, as is expected for such a three-center, four-electron π-system. Interestingly, the two minima above and below the CC double bond are deeper than those near the nitrogen atom *(Table 4)*. Moreover, at larger separations from **1b**, the only regions of maximum electrostatic attraction occur above and below the β-carbon atom. Thus, given a planar and rigid vinyl amine, charge control would initially direct a proton towards the β-carbon atom. At shorter distances from the molecular plane ($d \sim 1.5$ Å) the proton is drawn more towards the center of the CC double bond, and channels to the secondary minima near the nitrogen atom appear.

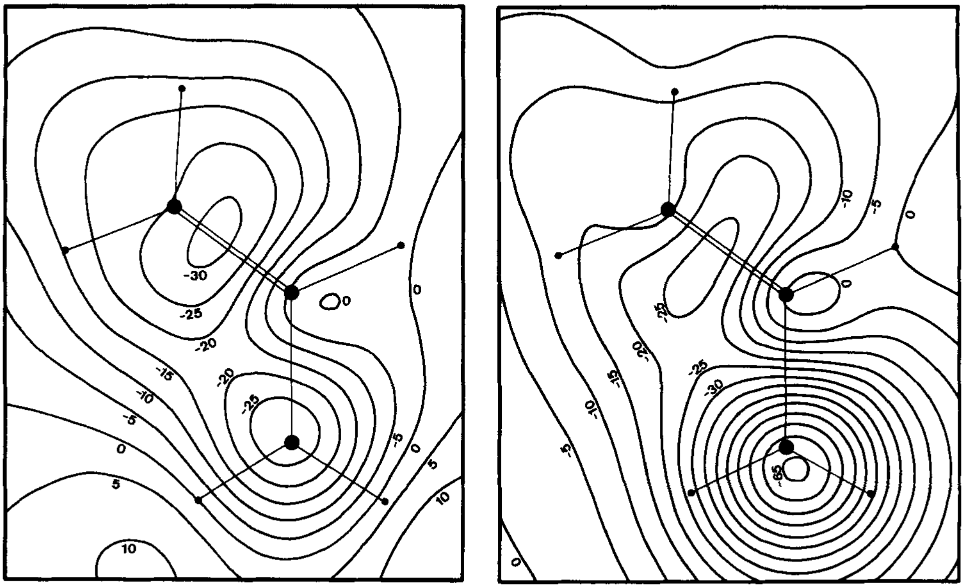


Figure 3. *Electrostatic potentials of vinyl amine with respect to a positive point charge. Equipotential curves through planes parallel to the CCN plane at a distance of d = 1.292 Å for the all-planar structure* **1b** *(left) and of d = 1.220 Å for the non-planar equilibrium configuration* **1a** *(right).* All energies in kcal/mol.

The situation is strikingly different for the non-planar equilibrium structure **1a**. Here the nitrogen atom is by far the most electrostatically favorable site for proton attack. The depth of the secondary potential minimum on the *exo* face of the CC double bond (*syn* to the nitrogen lone pair orbital) is comparable to that in **1b**, whereas that on the *endo* face is considerably reduced due to the proximity of the positively charged[8]) amino hydrogen atoms. Since the overall electronic distribution, as judged from a *Mulliken* population analysis, does not change dramatically in going from **1b** to **1a**[9]), it is the anisotropic distribution of the lone pair electrons at the pyramidal nitrogen atom which is mainly responsible for the prominence of the potential minimum at the nitrogen site. Interestingly, this minimum lies nearly on the axis of the localized[10]) nitrogen lone pair orbital, which in turn almost coincides with the axis through the nitrogen atom having equal angles to the N–C and the N–H bonds. At larger separations from the CCN plane (d ~ 4 Å) the attractive electrostatic potential centers above the C–N bond region. From there the proton entry channel leads towards the nitrogen atom and branches only at relatively short distances (d ~ 1.5 Å) to the secondary minimum above the CC double bond.

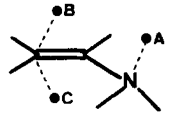
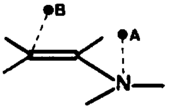
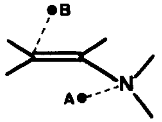
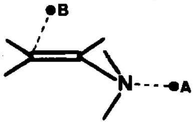
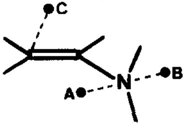
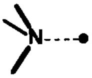
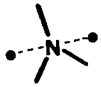
---

[8]) According to a *Mulliken* population analysis the two amino hydrogen atoms carry net charges of +0.192 and +0.189.

[9]) The gross atomic populations at the nitrogen and the α- and β-carbon atoms in **1a** and **1b** are, respectively, 7.368, 6.060, 6.342 and 7.393, 6.038, 6.363.

[10]) Localization was carried out according to the *Foster-Boys* criterion [25].

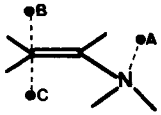
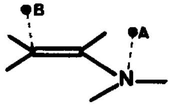
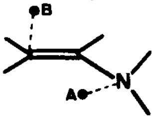
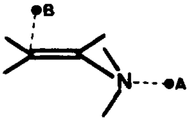
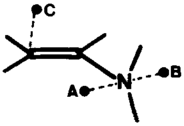
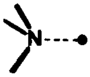
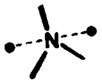
Table 4. *Energies and locations of electrostatic potential minima*[a]) *for vinyl amine, ammonia, and ethylene with respect to a positive point charge*

Structure		Site	E_{min}	r	γ	τ
1a		A	−74.7	1.061	105.5	−97.6
		B	−30.4	1.534	69.3	83.9
		C	−22.3	1.479	72.9	−99.6
1b		A	−30.1	1.197	85.5	−87.7
		B	−32.4	1.458	72.6	90.7
1c		A	−97.5	1.019	110.6	0
		B	−19.9	1.574	68.5	80.0
1d		A	−95.9	1.020	110.9	180
		B	−15.3	1.592	67.5	102.5
1e		A	−45.6	1.124	91.1	0
		B	−44.3	1.127	91.2	180
		C	−19.9	1.541	67.3	91.2
C_{3v}			−107.4	1.008	-	-
D_{3h}			−56.1	1.096	-	-
			−19.9	1.600	65.4	-

[a]) Energies in kcal/mol; specification of minima positions with respect to the heavy-atom skeleton in terms of the distance, r, to the nearest heavy atom, the pseudo-bond angle γ, and the torsional angle τ.

Proton addition to vinyl amine induces considerable charge reorganization within the nucleophile as well as charge transfer from the nucleophile to the proton. What are the consequences of these electronic relaxation effects? Inspection of vertical proton affinities calculated for **1a** and **1b** *(Table 5)* reveals that, by and large, the above electrostatic picture is retained, although some distinct modifications should be noted. For planar vinyl amine protonation of the CC double bond is still, and even more, favored over *N*-protonation. However, the best location for the proton is no longer above the center of the double bond but rather above the β-carbon atom. For the non-planar equilibrium structure **1a** inclusion of electronic relaxation effects merely results in a reinforcement of the strong electrostatic preference for *N*-protonation, the proton being pulled

Table 5. *Values and locations of maximum vertical proton affinities (PA_V)[a]) for vinyl amine, ammonia, and ethylene*

Structure		Site	PA_V	r	γ	τ
1a		A	246.7	1.045	110.6	−98.4
		B	196.0	1.174	90.9	87.5
		C	197.9	1.166	90.5	−95.2
1b		A	207.8	1.068	95.4	−90.4
		B	212.1	1.160	92.2	91.8
1c		A	256.2	1.041	114.2	0
		B	165.1	1.224	80.2	89.8
1d		A	255.0	1.041	113.8	180
		B	162.4	1.219	81.3	92.4
1e		A	222.5	1.062	95.4	0
		B	222.8	1.062	95.0	180
		C	166.6	1.224	79.4	91.1
C_{3v}			256.4	1.039	-	-
D_{3h}			229.5	1.063	-	-
			157.3	1.395	61.5	-

[a]) PA_V's in kcal/mol; specification of the positions of maximum PA_V with respect to the heavy-atom skeleton in terms of the distance, r, to the nearest heavy atom, the bond angle γ, and the torsional angle τ.

in further towards the nitrogen atom more or less along the axis of the lone pair orbital. Regarding *C*-protonation the proton again prefers to be right above or below the β-carbon atom rather than above or below the center of the CC double bond. More importantly, however, electronic relaxation effects favor protonation of the double bond from the sterically more crowded *endo* face, *i.e.*, *anti* to the nitrogen lone pair orbital. In fact, whereas electrostatic potential minima indicate an 8 kcal/mol preference for *exo* over *endo* attack of the double bond, vertical proton affinities favor *endo* over *exo* protonation by about 2 kcal/mol. The inference that without nuclear relaxation in the non-planar equilibrium structure of vinyl amine proton addition to the nitrogen and the β-carbon atom should occur preferentially from opposite sides of the molecule is of particular interest in view of continuing discussions concerning similar alternations in the stereochemical mode of substitution and elimination reactions involving allylic systems [4] [26] [27].

It is instructive to compare the electrostatic potential minima and the vertical proton affinities obtained for **1a** and **1b** with those calculated for the non-equilibrium configurations **1c**-**1e** as well as ammonia and ethylene. In **1c**-**1e** the nitrogen lone pair orbital is orthogonal to the double bond π-system so that the amino group may be expected to be essentially decoupled from the double bond. Indeed, there is a striking similarity between the patterns of either electrostatic potential minima or vertical proton affinities for **1c**-**1e** on the one hand and ammonia and ethylene on the other hand (*Tables 4* and *5*). By contrast, a considerable amount of lone pair delocalization into the double bond occurs in **1a** and **1b**, whereby electron density is shifted from the amino group to the double bond. As a result, both electrostatic attractions and vertical proton affinities for **1a** and **1b** are reduced at the nitrogen site, but enhanced at the CC double bond, relative to **1c**, **d** and **1e**, respectively.

Thus far, structural changes in vinyl amine which occur upon protonation have not been taken into account. Their influence on the relative site preference for proton attack can be assessed by examining the energies of the fully optimized *C*- and *N*-protonated species **2** and **3**. Proton addition to the pyramidal nitrogen atom of vinyl amine induces comparatively small structural changes within the nucleophile so that little relaxational energy gain is expected. In fact, the *N*-proton affinity of **1** is calculated to be 251.2 kcal/mol, which is only some 4.5 kcal/mol higher than the corresponding vertical proton affinity. Proton addition to the β-carbon atom of **1**, however, involves the conversion of a trigonally planar carbon atom to a tetrahedral one and the transformation of a pyramidal amino group into a planar immonium unit, resulting in a considerable relaxational energy gain of 63.0-64.9 kcal/mol[11]), as judged from the *C*-proton affinity of 260.9 kcal/mol calculated for **1**. PRDDO thus predicts *C*-protonated vinyl amine to be thermodynamically favored over the *N*-protonated form, the energy difference of 9.7 kcal/mol being somewhat smaller than that of 16.2 kcal/mol [28] based on 4-31G *ab initio* SCF MO calculations[12]).

Our model calculations suggest the following description of proton addition to simple aliphatic enamines. If such enamines were planar, electrostatic forces would tend to direct the proton towards the β-carbon atom. Electronic relaxation effects, in particular charge transfer to the proton at short distances, would further assist in the addition to this center, and geometric relaxation within the enamine would eventually lead to the thermodynamically favored methyl immonium derivative. However, as indicated by X-ray diffraction studies [4] [31], aliphatic enamines, as vinyl amine itself, tend to adopt non-planar structures with varying

---

[11]) The lower value refers to *endo* attack at the CC double bond, the higher to *exo* attack.

[12]) This energy difference is 17.3 kcal/mol from STO-3G calculations [28] but 32.0 kcal/mol using the CNDO/2 method [5]. For further comparison, the preference for acetaldehyde over vinyl alcohol has been estimated theoretically and experimentally to be 11.7 kcal/mol [29] and 13.2 kcal/mol [30], respectively.

degrees of pyramidality at the nitrogen atom and concomitant torsion around the C–N bond. With increasing non-planarity of the enamine unit, electrostatic forces at the nitrogen site are rapidly intensified and become the predominant factor directing the proton towards this center. Provided that nuclear relaxation within the enamine sets in relatively late in the addition process, the proton will have no chance to escape this entry channel, which ultimately leads to the thermodynamically less favored vinyl ammonium derivative[13]. Although this model description pertains to the gas-phase, it provides a rationale for the experimental observation that, in general, for aliphatic enamines in solution *N*-protonation is kinetically favored, whereas *C*-protonation occurs under conditions of thermodynamic control [1] [3].

Two problems remain to be solved. The first concerns the existence of a low-energy pathway for an intramolecular proton shift from the nitrogen to the more favorable carbon site. In view of the results of a recent theoretical study [29] on the transformation of vinyl alcohol to acetaldehyde, it seems rather unlikely that such a pathway is available in the case at hand. Bimolecular and/or solvent assisted processes would then be necessary to establish the thermodynamic equilibrium for protonated enamines, as indeed appears to be the case [1]. The second problem relates to the cooperation of geometric relaxation within the nucleophile during the protonation process. Information, as yet unavailable, specifying at what stage in this process such relaxations become decisive, is required for a more definitive discussion of the stereochemistry of proton addition to enamines. The solution of both problems calls for a detailed examination of the reaction hypersurface for the protonation of vinyl amine. Such studies are actively being pursued.

This work was partly supported by *Hoffmann-La Roche & Co.* (Basel). One of us *(L.D.B.)* wishes to thank the *Swiss National Science Foundation* for a postdoctoral fellowship. A generous grant of computing time by the ETHZ computing center is gratefully acknowledged.

REFERENCES

[1] *A.G. Cook*, Ed., 'Enamines: Synthesis, Structure, and Reactions', Marcel Dekker, New York 1969.
[2] *S.F. Dyke*, 'The Chemistry of Enamines', Cambridge University Press, London 1973.
[3] *M. Liler*, Adv. phys. org. Chemistry *11*, 267 (1975).
[4] *K.L. Brown, L. Damm, J.D. Dunitz, A. Eschenmoser, R. Hobi & C. Kratky*, to be published.
[5] *J. Teysseyre, J. Arriau, A. Dargelos & J. Elguero*, J. Chim. phys. *72*, 303 (1975).
[6] *J. Teysseyre, J. Arriau, A. Dargelos, J. Elguero & A.R. Katritzky*, Bull. Soc. chim. Belg. *85*, 39 (1976).
[7] *F.J. Lovas, F.O. Clark & E. Tiemann*, J. chem. Physics *62*, 1925 (1975).
[8] *R. Meyer*, Chimia *31*, 55 (1977).
[9] *R. Meyer*, Helv. *61*, 1418 (1978).

---

[13] Interestingly, attempts [5] to calculate protonation paths for vinyl amine by fixing the incoming proton on concentric spheres around either the nitrogen or the β-carbon atom did not yield a reaction path leading to the *C*-protonated derivative but only one leading to the *N*-protonated form.

[10] *T.A. Halgren & W.N. Lipscomb,* J. chem. Physics *58,* 1569 (1973).
[11] *J.A. Nelder & R. Mead,* Computer J. *7,* 308 (1964/5).
[12] *K. Müller & L. D. Brown,* unpublished work.
[13] *R.M. Stevens,* J. chem. Physics *55,* 1725 (1971).
[14] *S. Skaarup, L.L. Griffin & J.E. Boggs,* J. Amer. chem. Soc. *98,* 3140 (1976); *A. Schmiedekamp, S. Skaarup, P. Pulay & J.E. Boggs,* J. chem. Physics *66,* 5769 (1977).
[15] Landolt-Börnstein, 'Numerical Data and Functional Relationships in Science and Technology', New Series, Vol. *II/7,* Springer-Verlag, Berlin 1976.
[16] *D.R. Lide, Jr. & D. Christensen,* J. chem. Physics *35,* 1374 (1961).
[17] *K. Takagi & T. Kojima,* J. phys. Soc. Japan *30,* 1145 (1971).
[18] *L. Radom & J.A. Pople,* MTP Int. Rev. Sci. Phys. Chemistry, Series One, *1,* 71 (1972); *W.A. Lathan, L.A. Curtiss, W.J. Hehre, J.B. Lisle & J.A. Pople,* Progr. phys. org. Chemistry *11,* 175 (1974).
[19] *J.D. Swalen & J.A. Ibers,* J. chem. Physics *36,* 1914 (1962).
[20] *M. Tsuboi, A.Y. Hirakawa & K. Tamagake,* J. mol. Spectrosc. *22,* 272 (1967).
[21] *E. Hirota,* J. chem. Physics *45,* 1984 (1966).
[22] *W.G. Fateley & F.A. Miller,* Spectrochim. Acta *17,* 857 (1961).
[23] *R.W. Kilb, C.C. Lin & E.B. Wilson, Jr.,* J. chem. Physics *26,* 1695 (1957).
[24] *G. Klopman,* J. Amer. chem. Soc. *90,* 223 (1968).
[25] *J.M. Foster & S.F. Boys,* Rev. mod. Physics *32,* 300 (1960).
[26] *G. Stork & W.N. White,* J. Amer. chem. Soc. *78,* 4609 (1956); *G. Stork & F.H. Clarke,* ibid. *78,* 4619 (1956); *J.J. Uebel, R.F. Milaszewski & R.E. Arlt,* J. org. Chemistry *42,* 585 (1977).
[27] *K. Fukui & H. Fujimoto,* Bull. chem. Soc. Japan *40,* 2018 (1967); *W. Drenth,* Rec. Trav. chim. Pays-Bas *86,* 318 (1967); *N.T. Anh,* Chem. Commun. *1968,* 1089; *R.L. Yates, N.D. Epiotis & F. Bernardi,* J. Amer. chem. Soc. *97,* 6615 (1975).
[28] *F. Jordan,* J. phys. Chemistry *80,* 76 (1976).
[29] *W.J. Bouma, D. Poppinger & L. Radom,* J. Amer. chem. Soc. *99,* 6443 (1977).
[30] *J.L. Holmes, J.K. Terlouw & F.P. Lossing,* J. phys. Chemistry *80,* 2860 (1976).
[31] *M.P. Sammes, R.L. Harlow & S.H. Simonsen,* J. chem. Soc. Perkin II *1976,* 1126.

---

142. The Inversion of the Amino Group in Vinylamine, a Flexible Model Treatment[1]

by **Rolf Meyer**

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule,
Universitätsstrasse 22, CH-8092 Zürich

(10.III.78)

Summary

Flexible model results for the $-NH_2$ inversion in vinylamine are compared with microwave data published by *Lovas et al.* [3]. The information available on the spacing of inversion levels is found to be sufficient to rule out a planar equilibrium structure. Shifts of rotational constants upon excitation of the inversion are calculated for two predicted paths of motion derived from PRDDO geometry optimiza-

---

[1] A preliminary account of this work was given at the meeting of the *Swiss Chemical Society* in Geneva, October 9, 1976.