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

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(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-

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

tion results obtained by *Müller & Brown* [2]. Partial geometry optimization yields a path inconsistent with experiment but the path obtained from complete optimization produces shifts in excellent agreement with the observed shifts. A potential energy function compatible with experimental data on spacing of inversion levels is calculated from the observed inertia defects. The inversion angle at equilibrium is slightly smaller than the angle predicted from PRDDO calculations, and the barrier to inversion, $\Delta V = 1.08 \pm 0.07$ kcal/mol, is approximately half the PRDDO value.

Introduction. - Vinylamine is of considerable interest in organic chemistry as the prototype of enamines [1]. Its properties have been studied by quantum chemistry [2] while experimental data are scarce owing to the instability of this molecule. Only recently, microwave data including excited state spectra have been published by *Lovas et al.* [3]. These data are relevant to the question of planarity and to the type of motion associated with NH_2-inversion. They allow to test quantum chemical predictions and are therefore most useful in assessing the reliability of such calculations. A non-planar equilibrium structure was indicated by the observed inertia defect [3]. Independent evidence for a pyramidal NH_2-group is provided, as shown below, by the experimental information available on the inversion levels even though the observed data are rather inaccurate. Furthermore, two predicted paths of motion associated with inversion are studied by comparing calculated with observed shifts of rotational constants from the ground state to the first excited inversion state. Two predictions for the path of motion were derived from quantum chemical results obtained by *Müller & Brown* [2] using the PRDDO method [4]. One of these paths, which allows for partial structural relaxation, is found to be inconsistent with experiment while the path related to complete geometry optimization results yields excellent agreement.

For a model involving a given path of motion and the respective potential energy function, spectral data are calculated by the flexible model approach [5] for one degree of freedom of intramolecular motion. Such a model allows for variation of any structural parameter S_t as a function of a collective variable x ranging from $-\pi$ to π. The set of function $S_t = S_t(x)$ $(t = 1, 2, \ldots, 3N-6)$ to be specified for a given model defines the path of motion. Wavefunctions and energy levels are calculated for overall angular momentum quantum numbers $J=0$ and $J=1$, using a direct numerical method [5]. The calculated levels are used in analysing the experimental internal motion spectra and the observed rotational constants for the ground state as well as for excited states of the respective intramolecular motion. The calculated data to be compared with observed ones are consistent with the underlying model to a precision exceeding the experimental accuracy [5].

Pyramidal NH_2-Structure from Inversion Levels. - A non-planar equilibrium structure of vinylamine was indicated by the inertia defect of the ground state observed by *Lovas et al.* [3]. Evidence for a pyramidal NH_2-group can also be obtained from an analysis of the experimental information on the inversion levels[2]) E_1 and E_2 provided by the same workers [3]:

$$E_1 - E_0 = 65 \pm 25\ \mathrm{cm}^{-1} \qquad E_2 - E_0 > 200\ \mathrm{cm}^{-1}.$$

These data are rather inaccurate but are still sufficient to rule out a planar NH_2-group at equilibrium. This was found from a series of model calculations for NH_2-inversion. The inversion coordinate γ was defined by the dihedral angle between the CNH planes, as shown in *Figure 1*. It was related to the collective coordinate x by

$$\gamma = (124/180)\,\mathrm{x} \qquad (-\pi \leq \mathrm{x} \leq \pi)$$

which restricted its range to ±124°. Upon going from the planar configuration ($\gamma = 0$) to a pyramidal NH_2-group the CNH valence angles were assumed to decrease from 120° at $\gamma = 0$ to tetrahedral angles at $\gamma = 60°$,

$$\alpha_{237} = \alpha_{238} = 120° - 10.53°\,(\gamma/60°)^2.$$

Furthermore, as the NH_2-torsion[3]) is likely to combine with the inversion, three different assumptions were considered for such combination (see *Fig. 1*):

path 1: NH bond *syn* to double bond remains in CCN plane: $\tau_7 = 0$

path 2: both NH bonds are displaced from CCN plane by equal amounts: $\tau_7 = \gamma/2$

path 3: NH bond *anti* to double bond remains in CCN plane: $\tau_7 = \gamma$.

The calculation of wavefunctions and energy levels for $J = 0$ was efficient enough to allow for screening of potential parameters for all three cases. Upon going from the planar to a pyramidal configuration the kinetic energy coefficient $g^{\gamma\gamma}(\gamma)$ decreases as shown in *Figure 2*. Therefore the results calculated for a square well potential yielded $E_2 - E_0 < 2(E_1 - E_0)$ which disagrees with the condition $E_2 - E_0 > 2(E_1 - E_0)$ obtained from experiment. In addition, a square well potential compatible with a spacing $E_1 - E_0$ as low as the experimental upper

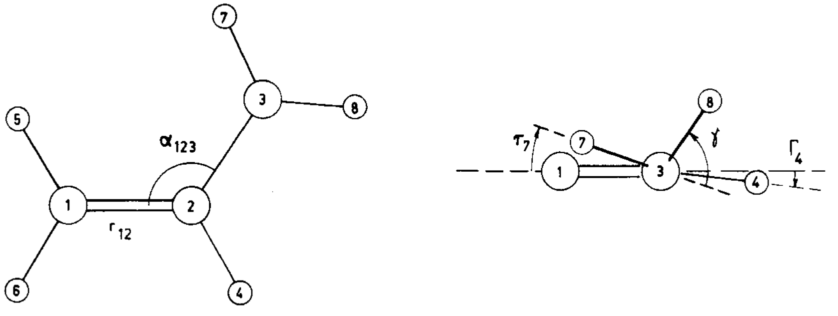

Fig. 1. *Vinylamine, definition of internal coordinates*

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[2]) E denotes molecular energy divided by hc.

[3]) The angles used in [2] are related to τ_7 and γ by $\phi = -\gamma/2$ and $\theta = \gamma/2 - \tau_7$.

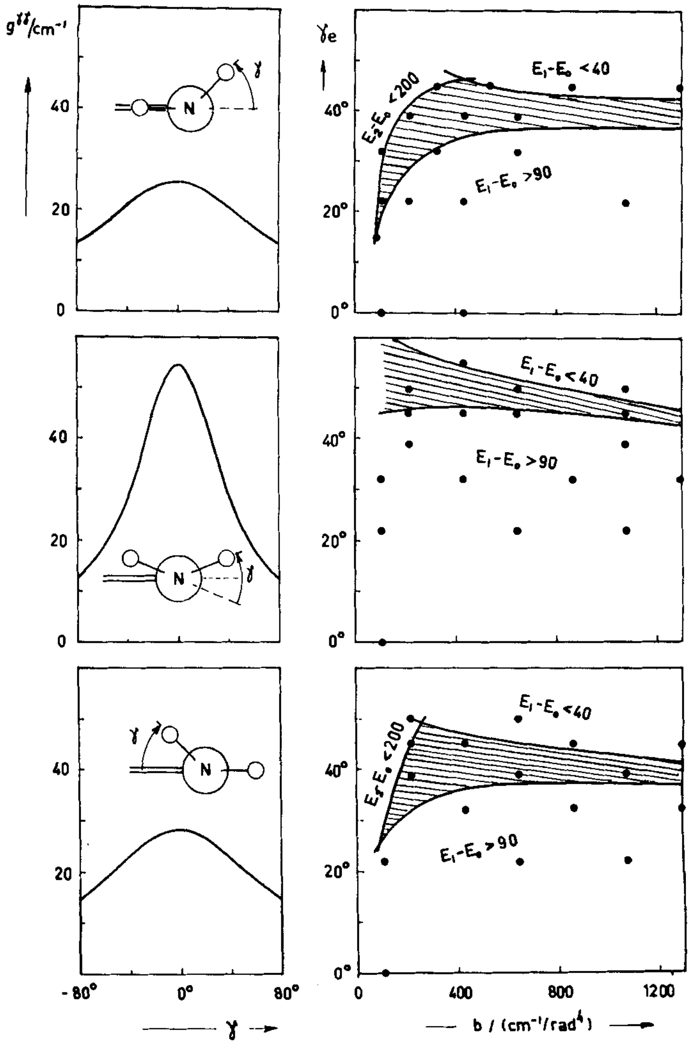

Fig. 2. *Vinylamine: Evidence for pyramidal NH_2-group from observations* $E_1-E_0=65\pm25$ cm^{-1} *and* $E_2-E_0>200$ cm^{-1} *for inversion levels.* For three different paths of motion, the kinetic energy coefficient is plotted (left), and ranges of the equilibrium coordinate for varying quartic potential parameter b are shown as shaded areas (right). Dots indicate calculated points.

limit of 90 cm^{-1} was found to be very shallow, such that inversion amplitudes turned out to be unrealistically large. With a purely quartic well the condition $E_2-E_0>2(E_1-E_0)$ could be fulfilled but the wavefunctions still decayed only beyond $\gamma=\pm90°$ if the spacings E_1-E_0 were required not to exceed 90 cm^{-1}. A fourth order potential function with a positive quadratic term was therefore ruled out as incompatible with experiment and/or physically unrealistic. Hence the potential function was assumed as

$$V(\gamma)=-a\gamma^2+b\gamma^4 \qquad (a\geq0, b>0),$$

and the range of parameters a, b compatible with observed data was explored numerically for all three assumed paths of motion. The corresponding ranges for the equilibrium angle and for the barrier are obtained, respectively, from

$$\gamma_e=(a/2\,b)^{1/2} \qquad \text{and} \qquad V(0)-V(\gamma_e)=b\gamma_e^4\,.$$

The results of these calculations are shown in *Figure 2*. Lower bounds to b-values arising from the condition $E_2-E_0>200$ cm^{-1} are shown for paths 1 and 3. Inversion amplitudes, however, were found to be already unacceptably large near these bounds. For this reason, b-values below 200 cm^{-1}/rad^4 should be rejected. Thus the angle γ_e is definitely greater than 20° and may be expected to lie in the range 35°-55° if b is larger than 400 cm^{-1}/rad^4. This result lends independent support for a non-planar NH_2-structure, in addition to the evidence from the observed inertia defect [3].

Path of Motion. - Obviously the experimental data are not sufficient to determine the actual path of motion associated with inversion, but they still allow tests of theoretical predictions concerning this path. For vinylamine two such predictions were obtained from quantum chemical calculations using the PRDDO approach [2]. In a preliminary series of calculations the NH_2-torsional coordinate was optimized for different inversion angles while making the assumption stated above for the CNH angles (see *Fig. 1* of [2]). This yielded a barrier to inversion of 1.6 kcal/mol and equilibrium coordinates $\gamma_e=46°$ and $\tau_{7e}=15.6° \approx \gamma_e/3$ (see *Fig. 1*), which indicated an intermediate motion between paths 1 and 2 assumed above. A "partial relaxation model" was based on an interpolation of these results and on a reference structure close to the one given by *Lovas et al.* [3]:

partial relaxation path (see *Fig. 1*)

variable: $\gamma=(124/180)\,x$

$\tau_7=\gamma/3, \qquad \alpha_{237}=\alpha_{238}=120°-10.53°\,(\gamma/60°)^2$

constant:

$$r_{37}=r_{38}=1.000\,\text{Å}, \quad r_{15}=r_{16}=r_{24}=1.090\,\text{Å}, \quad r_{12}=1.335\,\text{Å}, \quad r_{23}=1.400\,\text{Å},$$
$$\alpha_{215}=\alpha_{216}=121.0°, \quad \alpha_{124}=123.0°, \quad \alpha_{123}=125.0°,$$

planar $CH_2{=}CHN$ structure.

A second model was defined from the completely optimized geometries for the equilibrium structure and for a CNH_2-configuration restricted to planarity. Both geometries were calculated by *Müller & Brown* [2] using the PRDDO method which yielded energy minima for $\gamma=\pm 53.5°$ and a barrier of 2.37 kcal/mol. Again the corresponding path of motion was defined by interpolation:

complete relaxation path (see *Fig. 1*)

variable:

$\gamma=(124/180)\,x, \qquad \alpha_{237}=121.39°-7.68°\,(\gamma/53.5°)^2,$

$\tau_7=18.7°\,(\gamma/53.5°), \qquad \Gamma_4=3.7°\,(\gamma/53.5°) \qquad \alpha_{238}=122.09°-7.86°\,(\gamma/53.5°)^2,$

$r_{12} = 1.342\ \text{Å} - 0.003\ \text{Å}\ (\gamma/53.5°)^2$,
$r_{23} = 1.391\ \text{Å} + 0.025\ \text{Å}\ (\gamma/53.5°)^2$,
$r_{15} = r_{16} = 1.089\ \text{Å} + 0.002\ \text{Å}\ (\gamma/53.5°)^2$,
$r_{37} = 1.015\ \text{Å} + 0.009\ \text{Å}\ (\gamma/53.5°)^2$,
$r_{38} = 1.014\ \text{Å} + 0.011\ \text{Å}\ (\gamma/53.5°)^2$,

$\alpha_{124} = 120.79° + 0.08°\ (\gamma/53.5°)^2$,
$\alpha_{215} = 122.06° - 0.25°\ (\gamma/53.5°)^2$,
$\alpha_{216} = 122.17° + 0.24°\ (\gamma/53.5°)^2$,
$\alpha_{123} = 126.08° - 0.38°\ (\gamma/53.5°)^2$;

constant: $r_{24} = 1.101\ \text{Å}$,

vinyl group (CH_2=CH) remains planar.

The potential energy function $V = -a\gamma^2 + b\gamma^4$ derived from the quantum chemical results $\gamma_e = 53.5°$ and $V(0) - V(\gamma_e) = 2.37$ kcal/mol turned out to be inconsistent with the experimental range for $E_1 - E_0$. Therefore only the paths of motion were taken as predicted while the two potential parameters were adjusted on the basis of the inertia defects Δ_0 and Δ_1 observed for the ground state and for the first excited inversion state, respectively. Energy levels and rotational constants obtained in this way for partial and complete relaxation are shown in the *Table*. The data include the second moments defined by

$$(M_{aa})_v = \frac{1}{2}(-1/A_v + 1/B_v + 1/C_v) \approx (\sum m a^2)_v,$$

$$(M_{bb})_v = \frac{1}{2}(1/A_v - 1/B_v + 1/C_v) \approx (\sum M b^2)_v,$$

$$(M_{cc})_v = \frac{1}{2}(1/A_v + 1/B_v - 1/C_v) \approx (\sum m c^2)_v, \quad (M_{cc})_v = -\frac{1}{2}\Delta_v.$$

For a given state v these quantities represent apparent mass dispersions along the respective principal axes and are therefore related more directly to the "effective" molecular geometry than the rotational constants.

The calculated ground state rotational constants agree with the observed ones within at most 1 per cent in the case of partial relaxation. To some extent this agreement is due to adjustments made for the CN distance and the CCN-bond angle [3]. By contrast the complete relaxation model is based exclusively on geometrical data from quantum chemistry, with the only exception of the equilibrium value of the inversion angle. Nevertheless the ground state rotational constants calculated for the complete relaxation case agree with the observed ones within not more than 1.4 per cent.

The most sensitive quantities to the path of motion are the shifts of the rotational constants from the ground state to the first excited state, which are also shown in the *Table*. For the partial relaxation path the calculated values for $A_1 - A_0$ are correct in sign but only about half the size of the observed shift. The shifts calculated for B and C disagree by more than a factor 4 in absolute value with the observed ones and the calculated change $B_1 - B_0$ is wrong in sign. These disagreements could not be lifted by any acceptable change in the potential function. Hence the partial relaxation path must be regarded as

Table. *Vinylamine NH_2-inversion levels* (E in cm^{-1}), *rotational constants* (MHz) *and second moments* (M in uÅ$_2$) *for ground state and shifts for first excited inversion state.* Equilibrium angles γ_e and barriers ($\Delta V = V(0) - V(\gamma_e)$ in kcal/mol) define quartic potential functions. Calculated data refer to partial relaxation ($-NH_2$ torsion, CNH angles) and complete relaxation paths predicted from PRDDO geometry optimization.

	Calculated				Observed[a]
	Partial relaxation[b]		Complete relaxation[b]		
γ_e	46°	46°	46°	48°	
ΔV	1.00	1.10	1.08	1.08	
E_0	−147.52	−168.45	−159.95	−167.49	
$E_1 - E_0$	65.02	61.42	66.95	56.67	65 ± 25
$E_2 - E_0$	377.87	395.47	406.41	378.75	> 200
Ground state					
A	55,787.74	55,776.02	56,037.40	55,914.17	56,312.9 ± 19.0
B	10,102.92	10,103.98	9,896.93	9,895.43	10,034.76 ± 0.06
C	8,603.10	8,604.44	8,457.82	8,459.46	8,564.93 ± 0.06
M_{aa}	49.854	49.846	50.899	50.887	50.197 ± 0.0015
M_{bb}	8.890	8.889	8.854	8.854	8.809 ± 0.0015
M_{cc}	0.169	0.172	0.065[c]	0.185	0.166 ± 0.0015
Shifts from ground to first excited state					
ΔA	−247.40	−229.19	−424.33	−420.96	−435 ± 42
ΔB	24.41	22.57	−5.09	−5.09	−5.10 ± 0.18
ΔC	31.56	29.15	4.93	5.06	5.10 ± 0.17
ΔM_{aa}	−0.188	−0.174	−0.038	−0.039	−0.040 ± 0.0034
ΔM_{bb}	−0.027	−0.025	0.003	0.003	0.005 ± 0.0034
ΔM_{cc}	0.067	0.062	0.165[c]	0.065[c]	0.065 ± 0.0034

[a] See [3]. [b] See [2]. [c] Adjusted to experimental values by choice of potential parameters.

inconsistent with the observed shifts of rotational constants. By contrast the results for the complete relaxation path coincide with the observed data within experimental error. As far as the effect on the shifts of rotational constants is concerned, the most important single contribution to the relaxation is the extension of the CN bond upon going from the planar to a pyramidal form. This extension reduces the change $(M_{aa})_1 - (M_{aa})_0$ from its value of about -0.18 uÅ^2 in the partial relaxation model towards the experimental change of -0.04 uÅ^2. Smaller reductions are due to the extension of the NH bonds and to the slower decrease of the CNH angles. A slight counteraction to this trend arises from the shrinking of the C=C bond and of the CCN angle. Similar considerations apply to the moment M_{bb}, *i.e.* to the mass dispersion along the principal axis b. On the other hand the moments $(M_{cc})_1$ and $(M_{cc})_0$ depend mainly on the shape of the potential function and on the out of plane relaxations given by $\tau_7(\gamma)$ and $\Gamma_4(\gamma)$. Since the individual contributions predicted from the quantum chemical calculation evidently add up to a path of motion consistent with experiment no attempt was made to introduce any modifications.

Potential Energy Parameters from Inertia Defect. - The parameters of the potential energy function were varied in order to investigate the sensitivity of the rotational constants. From the *Table* it is seen that M_{cc} and, hence, the inertia defect is strongly dependent on the equilibrium angle γ_e. In addition, the shift $\Delta M_{cc} = (M_{cc})_1 - (M_{cc})_0$ is sensitive to the barrier ΔV. These potential parameters were therefore determined by adjusting calculated to observed data for M_{cc}. According to the third column of the *Table* agreement is obtained for $\gamma_e = 46°$ and $\Delta V = 1.08$ kcal/mol. However, the observed value $(M_{cc})_0 = 0.166$ uÅ^2 may contain contributions not only from the inversion but from the vibrations as well. An estimate for this vibrational contribution may be obtained from the

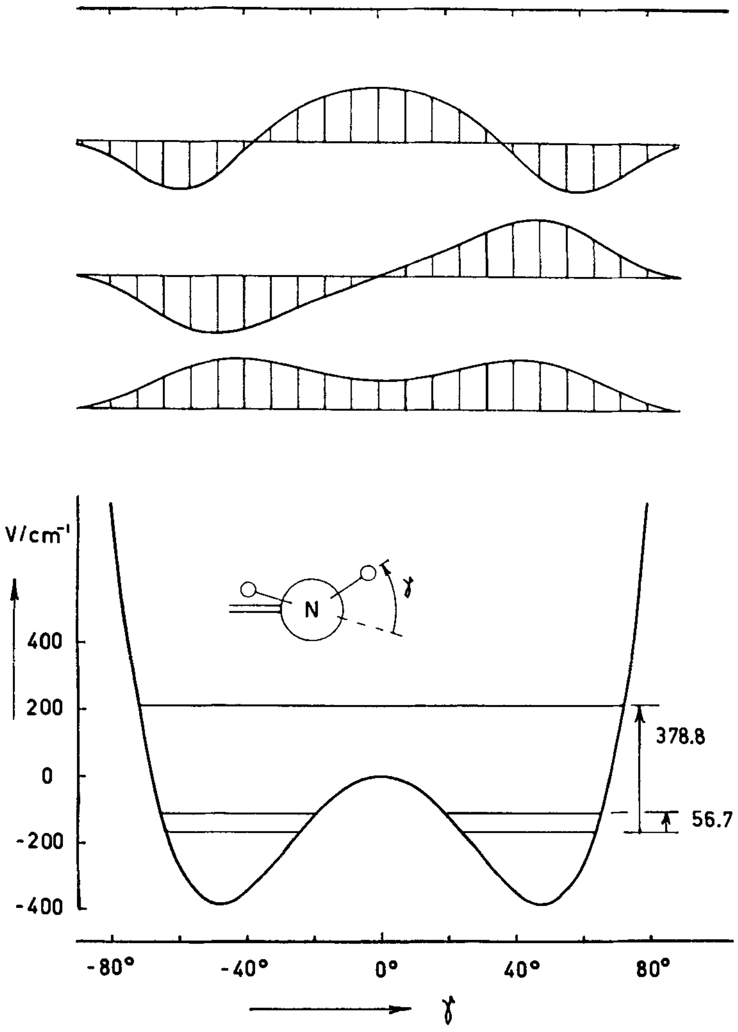

Fig. 3. *Inversion in vinylamine: Potential energy* $V = -a\gamma^2 + b\gamma^4$ *along complete relaxation path, energy levels, and wavefunctions*

inertia defect observed by *Saito* [6] for vinyl alcohol, the most closely related molecule lacking inversion. This inertia defect corresponds to a vibrational term of about -0.02 uÅ^2 in M_{cc}. If so, the term arising from inversion should be closer to 0.185 than 0.165 uÅ^2. This would yield a larger equilibrium angle, as assumed for the forth column of the *Table*. On the basis of an estimate -0.02 ± 0.01 uÅ^2 for the vibrational contribution the result for the equilibrium angle is

$$\gamma_e = 48° \pm 1°.$$

The barrier to inversion obtained from the shift $(M_{cc})_1 - (M_{cc})_0$ is

$$\Delta V = V(0) - V(\gamma_e) = 1.08 \pm 0.07 \text{ kcal/mol}$$

with error bounds corresponding to the experimental uncertainties. The respective potential function along the complete relaxation path, energy levels, and wavefunctions are shown in *Figure 3*.

In conclusion, one may note that the complete relaxation model allows determination of a potential function from inertia defects, which is consistent with experimental information on inversion frequencies. Whatever shortcomings of the PRDDO method may be responsible for its relatively poor results for the inversion barrier, its results for complete geometry optimization in vinylamine have yielded surprisingly good agreement with experiment for the rotational constants of the ground state and, in particular, for their changes upon excitation of the inversion.

Support of this work by the *Swiss National Science Foundation* (Project Nrs. 2.519-0.76, 2.712-0.77) and a generous grant of computation time by the ETHZ computation center are gratefully acknowledged.

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