

the cyclic hexapeptides I and II, it appears that the conformations of an isolated L-proline residue and residues with a β carbon in the side chain which precede L-proline may be locked into single conformations or average conformations, after incorporation into a growing protein. The steric barriers to inter conversion between minimum A and C in an isolated L-proline residue and between α -helical and non- α -helical conformations in a β -carbon containing residue preceding L-prolyl would seem sufficient to maintain these residues in the conformations in which they were synthesized into the protein. On the other hand, the barrier to cis-trans isomerization^{34a} of the imide bond in an L-proline residue does not appear to be as formidable.^{16,31} There are no such severe steric barriers present in the calculated¹⁻⁶ conformational energy maps for nonprolyl L residues which are not succeeded by L-proline.

Since protein synthesis involves³⁵ the stepwise addition of single amino acids beginning with the N-terminal amino acid or peptide residue, how does the residue with a β -carbon side chain in the process of attachment to the growing protein chain know whether to adopt α -helical or non- α -helical conformations when the following residue to be incorporated is an L-proline? For that matter, how does the newly attached L-prolyl residue know whether to adopt conformations corresponding to minimum A or minimum C, since the

(34) (a) It is of interest to note that *cis*-L-prolyl imide bonds have been postulated to account for certain conformational features of the proteins subtilisin BPN'^{34b} and ribonuclease S.^{34c} (b) C. S. Wright, R. A. Alden, and J. Kraut, *Nature (London)*, **221**, 235 (1969); (c) H. W. Wyckoff, K. D. Hardman, N. M. Allewell, T. Inagami, C. M. Johnson, and F. M. Richards, *J. Biol. Chem.*, **242**, 3984 (1967).

(35) (a) J. P. Watson, "Molecular Biology of the Gene," W. A. Benjamin, New York, N. Y., 1965, Chapters 11 and 13; (b) M. V. Volkenstein, "Molecules and Life," translated by S. N. Timasheff, Plenum Press, New York, N. Y., 1970, Chapter 7.

interconversion between them would appear to be difficult once the next peptide residue is added? In fact, only conformations corresponding to minimum C are possible⁷ if the next residue to be added is also L-prolyl. A possible explanation for the conformational preference suggested above may lie in the observed³⁵ degeneracy of the template ribonucleic acid (RNA) codons and the multiplicity of transfer RNA's required in the attachment of several of the amino acids in protein synthesis.

Finally, it appears that the combination of approximate conformational energy calculations and a Karplus-like relation connecting the dihedral angle and vicinal coupling constants between N-H and C $^{\alpha}$ -H $^{\alpha}$ in peptide residues enables the proposal of several conformations for the proline containing cyclic hexapeptides I and II, which are consistent with the conformation-dependent information obtained by nmr measurements performed in solution. Hexapeptide I apparently flips between two Gly-Gly hydrogen-bonded conformations, both of which have all-trans peptide bonds with minimum C prolines, by small rotation in the glycine residues. The minor component of hexapeptide I probably contains a single imide bond in the *cis* conformation. The proportion of major and minor hexapeptide I conformations appears to be independent of solvent. Hexapeptide II adopts at least two conformations, or average conformations, one with *trans* and the other with *cis* imide bonds whose proportions are solvent dependent. The *trans* imide bond conformation possesses strong internal Ser-Ser hydrogen bonds, while the *cis* imide bond conformation does not. Both conformations contain proline and serine residues in conformations corresponding to minimum C and non- α -helical regions of their conformational energy maps, respectively.

The N-N Torsional Potential Function in Methylhydrazine

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Abstract: The potential function hindering the N-N torsional motion in methylhydrazine has been determined using microwave and far-infrared spectroscopic data. The Fourier coefficients in the potential function, including three sine terms (a_k) and three cosine terms (b_k), are (in cm^{-1}): $a_1 = 73$, $a_2 = 21$, $a_3 = -87$, $b_1 = 569$, $b_2 = 967$, and $b_3 = 339$. These constants lead to a *trans* barrier height of $1253 \pm 25 \text{ cm}^{-1}$ ($3.58 \pm 0.07 \text{ kcal/mol}$) with the maximum at a torsional angle θ of 197° and a *cis* barrier height of $3028 \pm 300 \text{ cm}^{-1}$ ($8.66 \pm 0.86 \text{ kcal/mol}$) with the maximum at a θ value of 359° . The spectra were interpreted using a one-dimensional model in which the only motion is the torsion about the bond connecting the frame ($-\text{NH}-\text{CH}_3$) and the top ($-\text{NH}_2$). The far-infrared spectrum of methylhydrazine has been reinterpreted on the basis of the derived potential function. The spectroscopic entropy of methylhydrazine has been reexamined, and we have found our results to be consistent with the entropy determined experimentally from heat capacity measurements.

Barriers to internal rotation and relative stabilities of rotational isomers have been subjects of interest for a number of years. Although many different techniques have been employed,¹ the most accurate studies

(1) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

of hindered internal rotation have involved either microwave or far infrared spectroscopy, or a combination of these methods. Most of the microwave-far-infrared studies to date have involved molecules in which a symmetric-top group (usually $-\text{CH}_3$) is attached to a sym-

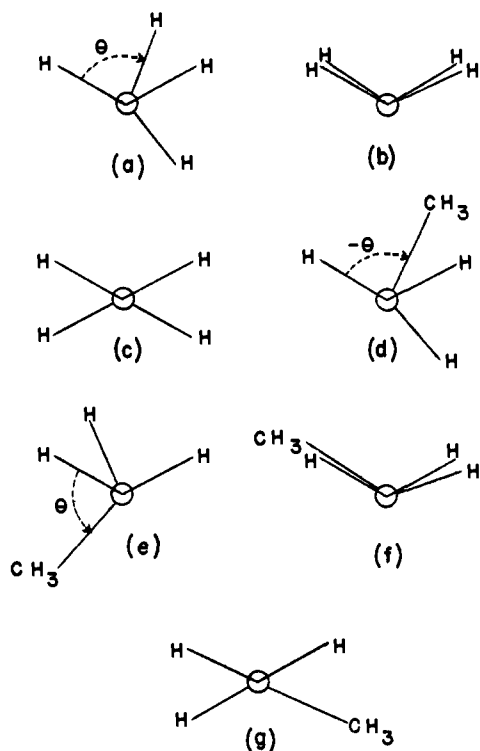
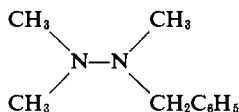


Figure 1. Rotamers of hydrazine and methylhydrazine as viewed along the N-N axis. For hydrazine the skew rotamer ($\theta \sim 90^\circ$) is shown in (a), the cis rotamer ($\theta = 0^\circ$) in (b), and the trans rotamer ($\theta = 180^\circ$) in (c). For methylhydrazine the inner skew rotamer ($\theta \sim -90^\circ$) is shown in (d), the outer skew rotamer ($\theta \sim 90^\circ$) in (e), the cis rotamer ($\theta \sim 0^\circ$) in (f), and the trans rotamer ($\theta \sim 180^\circ$) in (g).

metric or an asymmetric framework,² but there has recently appeared a small number of papers concerned with the more complicated problem of the rotation of two asymmetric groups bonded to each other.³ While most of the latter studies have involved internal rotation about the C-C bond, our interest has been that of restricted rotation about the N-N bond in methylhydrazine.

The subject is particularly topical since the parent hydrazine molecule has been recently the subject of *ab initio* potential surface calculations,⁴⁻⁶ and indeed the methylhydrazine molecule itself is currently being investigated theoretically.^{7,8} The subject has recently been of experimental interest, also. For example, Anderson, *et al.*,⁹ observed the temperature dependence of the nmr spectrum of



and analyzed the results in terms of the internal motions (inversions and N-N internal rotations) of the molecule.

- (2) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 841 (1959); R. M. Lees and J. G. Baker, *J. Chem. Phys.*, **48**, 5299 (1968).
 (3) V. W. Laurie, *Accounts Chem. Res.*, **3**, 331 (1970).
 (4) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1966).
 (5) W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967).
 (6) L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967).
 (7) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).
 (8) R. E. Christoffersen, private communication.
 (9) J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6371 (1969).

The far-infrared¹⁰ and microwave¹¹ spectra of methylhydrazine have previously been reported. The former study attempted to explain the N-N torsional spectrum of the molecule, but the results obtained are of questionable validity due to the assumption of an incorrect model (that of a symmetric threefold barrier) for the amino torsion. The latter study established the relative stabilities of the inner and outer skew rotamers and provided estimates of the effective torsional angles, θ_i and θ_o . It was felt that a better description of the amino torsional potential curve could be obtained by combining the data from these two studies.

The potential energy hindering an internal rotation can be expanded in a Fourier series

$$V(\theta) = V_0 + \sum_{k=1} a_k \sin k\theta + \sum_{k=1} b_k \cos k\theta \quad (1)$$

where θ is the torsional angle and V_0 is an arbitrary zero of potential energy. Projections showing θ in hydrazine and methylhydrazine are shown in Figure 1. The N-N torsional barrier in methylhydrazine is expected to be qualitatively similar to that of the parent hydrazine molecule. The correct form for the barrier in hydrazine (and for the O-O barrier in hydrogen peroxide) was first suggested by Penney and Sutherland,¹² who proposed a potential in which the dominant term is b_2 . In their model two potential maxima occur at the electron-pair cis ($\theta = 0^\circ$) and trans ($\theta = 180^\circ$) positions, with the cis position considerably higher in energy than the trans. Two equivalent skew minima were proposed at torsional angles of about $\pm 90^\circ$. The correctness of the Penney-Sutherland picture has been demonstrated recently in calculations based on microwave and far-infrared data for hydrogen peroxide,¹³⁻¹⁵ and recent *ab initio* calculations on the barrier in hydrazine also support this form of the potential.⁴⁻⁶ Kasuya estimated the barrier in hydrazine from splittings observed in the microwave spectrum,¹⁶ but his calculated value of 1100 cm^{-1} was based on an incorrect model which assumed the cis and trans barriers to be equal. The principal difference between the hydrazine and methylhydrazine barriers is that the two skew minima become nonequivalent for the latter molecule. In this paper we will describe an approximate method which may be used to make quantitative estimates, based on data from infrared and microwave spectroscopic studies, of the barrier hindering the amino torsion in the methylhydrazine molecule.

The Torsional Hamiltonian

General Form. We assume a form for the torsional Hamiltonian (H_T) similar to that derived previously for 3-fluoropropene¹⁷ and hydrogen peroxide¹⁴

$$H_T = -(1/4)[p_\theta^2 F(\theta) + F(\theta)p_\theta^2 + 2p_\theta F(\theta)p_\theta] + V(\theta) \quad (2)$$

- (10) J. R. Durig, W. C. Harris, and D. W. Wertz, *J. Chem. Phys.*, **50**, 1449 (1969).
 (11) R. P. Lattimer and M. D. Harmony, *ibid.*, **53**, 4575 (1970).
 (12) W. G. Penney and G. B. B. M. Sutherland, *ibid.*, **2**, 492 (1934).
 (13) R. L. Redington, W. B. Olson, and P. C. Cross, *ibid.*, **36**, 1311 (1962).
 (14) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, **42**, 1931 (1965).
 (15) R. H. Hunt and R. A. Leacock, *ibid.*, **45**, 3141 (1966).
 (16) T. Kasuya, *Sci. Pap., Inst. Phys. Chem. Res., Tokyo*, **56**, 1 (1962).
 (17) P. Meakin, D. O. Harris, and E. Hirota, *J. Chem. Phys.*, **51**, 3775 (1969).

where p_θ is the operator $d/d\theta$ and $F(\theta)$ is a quantity proportional to the inverse reduced moment of inertia for the torsion. In writing this expression we assume (1) that the torsional Hamiltonian is separable from the total molecular Hamiltonian, (2) that the effects of other internal motions (including inversions) may be neglected, and (3) that the torsional motion is expressible in terms of a one-dimensional variable, the torsional angle θ . The kinetic and potential energy parts are discussed separately below.

Assumptions 1-3 above represent simplifications of the problem which are not justifiable on any *a priori* basis. However, the microwave spectra of methylhydrazine¹¹ and hydrazine¹⁶ indicate that coupling of the N-N torsion with the other internal motions is reasonably small. Therefore the assumptions should represent the problem correctly to a first approximation. The use of such a one-dimensional model has led to satisfactory results in numerous other cases,^{3, 16, 17} although there are instances³ when coupling terms may be needed to describe adequately the nonrigid rotor character of microwave spectra.

The Kinetic Energy. We assume that the reduced moment of inertia (I_r) for the torsion may be expressed as¹⁸

$$I_r = \frac{h^2}{8\pi^2 F} = I_t \left(1 - I_t \sum_{i=1}^3 \frac{\alpha_i^2}{I_i} \right) \quad (3)$$

where I_t is the moment of inertia of the top ($-\text{NH}_2$) about the N-N axis, I_i is the moment of inertia of the whole molecule about the i th principal axis, and α_i is the direction cosine between the i th principal axis and the N-N axis. For methylhydrazine F is a function of θ and may be represented by a sum of rapidly convergent sine and cosine terms

$$F(\theta) = F_0 + F_1 \cos \theta + F_2 \sin \theta + \dots \quad (4)$$

From the molecular structure of methylhydrazine¹¹ we calculated values of I_i and α_i for several values of θ , and then $I_r(\theta)$ and $F(\theta)$ were determined from these. Fitting these points to eq 4 we obtain (in cm^{-1})

$$F = 10.395 - 0.012 \cos \theta + 0.025 \sin \theta \quad (5)$$

It is clear that F is only a very weak function of θ . For this reason it was believed that very little error would be introduced into the methylhydrazine energy expression by omitting the θ -dependent terms in the kinetic energy and thus neglecting the fact that F is really a function of θ . Consequently only the leading term in eq 5 was used in the barrier calculations.

The Potential Energy. Three cosine and three sine terms were used in a Fourier series (eq 1) to represent the potential energy for methylhydrazine. V_0 was chosen such that the zero of potential energy lies at the minimum of the lower energy skew well (the inner rotamer). The six remaining parameters were then adjusted so as to give eigenvalues in agreement with experimentally measured quantities. A general method for determining the values of these parameters

(18) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1953, p 482. Strictly speaking, eq 3 is valid only for the case in which at least one of the rotating groups is symmetrical with respect to the axis of internal rotation, or equivalently, in which I_r is not a function of θ . We assume eq 3 to be approximately true for $-\text{NH}_2$, since I_r for this group is only a weak function of θ .

has been discussed by Riveros and Wilson¹⁹ and hence will be considered only briefly here.

Two relationships were obtained from first derivative expressions, which require the derivative to be zero at the minima of the inner and outer skew wells

$$(dV/d\theta)_{\theta_i} = (dV/d\theta)_{\theta_o} = 0 \quad (6)$$

The remaining four parameters were adjustable in the calculations to give the best fit to experimental quantities. Two of these related the potential curve to the force constants (k_i and k_o) for each well, which in turn are related to the vibrational energies. As a first approximation, for the inner well

$$(d^2V/d\theta^2)_{\theta_i} = k_i \simeq 4\pi^2\nu_i^2(G_{tt}^{-1})_i \quad (7)$$

where ν_i is the fundamental frequency of the torsional vibration and $(G_{tt}^{-1})_i$ is the torsional element of the G^{-1} matrix.²⁰ A similar expression may be written for the outer well (θ_o). The final two parameters were energy difference expressions. One was the energy difference between the outer and inner minima

$$V_{\theta_o} - V_{\theta_i} = \Delta E_{o-i} \quad (8)$$

and the second parameter was the energy difference between the cis and trans configurations

$$V_{\theta=0^\circ} - V_{\theta=180^\circ} = \Delta E_{c-t} \quad (9)$$

In summary then, the variables for methylhydrazine were k_i , k_o , ΔE_{o-i} , and ΔE_{c-t} , with the additional requirement that $dV/d\theta$ be set equal to zero for the inner and outer well minima.

Potential Function

The determination of the Fourier coefficients was carried out using six principal pieces of experimental data. From the microwave study¹¹ the following quantities were used:²¹ $\theta_i = -84.5^\circ$, $\theta_o = 83.3^\circ$, and $\Delta E'_{o-i} = 293 \text{ cm}^{-1}$. From the infrared study of Durig, *et al.*,¹⁰ these frequencies (cm^{-1}) were taken:²² $\nu_i(0 \rightarrow 1) = 315.5$, $\nu_i(1 \rightarrow 2) = 289$, and $\nu_o(0 \rightarrow 1) = 257$. This gives a total of six experimental quantities to which the six independent Fourier coefficients can be adjusted. Additional infrared data are available, however, and some adjustments were made to provide the best overall fit to the microwave and infrared data.

The basis functions chosen for the calculations were $\{e^{\pm im\theta}\}$. Matrix elements of H_T were calculated using 41 basis functions, and the resulting matrix was diagonalized by a computer program written for the Honeywell 635 computer. Localized energy levels were identified by computing the probabilities of the various eigenstates in each potential well. Tests using smaller numbers of

(19) J. M. Riveros and E. B. Wilson, Jr., *J. Chem. Phys.*, **46**, 4605 (1967).

(20) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955; S. R. Polo, *J. Chem. Phys.*, **24**, 1133 (1956). It should be emphasized that the expression $(4\pi^2\nu^2 G_{tt}^{-1})$ was used only to determine an initial estimate of k , which was subsequently varied to give the best fit to the lower vibrational states.

(21) The prime (') is used here on ΔE_{o-i} because the microwave quantity is the difference in the ground state energy levels of the inner and outer rotamers, not the difference in the well minima, as is implied in eq 8.

(22) The assumed value of the $\nu_o(0 \rightarrow 1)$ transition is a reassignment of one of the lines in the far-infrared spectrum. The reasons for this reassignment are discussed in a later section.

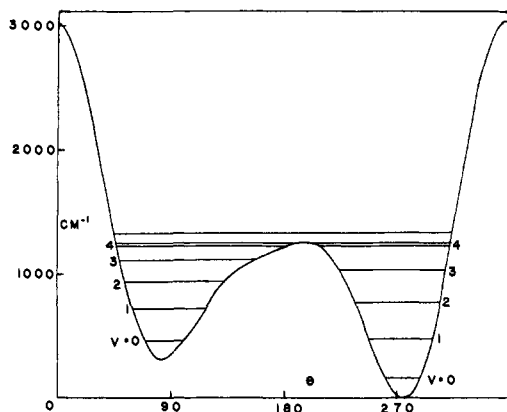


Figure 2. The hindering potential and energy levels of methylhydrazine.

functions indicated that 41 functions were sufficient for the convergence of the eigenstates of interest.

The final Fourier coefficients (cm^{-1}) are as follows: $a_1 = 73$, $a_2 = 21$, $a_3 = -87$, $b_1 = 569$, $b_2 = 967$, $b_3 = 339$. These coefficients yield a trans barrier height of 1253 cm^{-1} (3.58 kcal/mol) with the maximum at $\theta = 197^\circ$ and a cis barrier height of 3028 cm^{-1} (8.66 kcal/mol) with the maximum at $\theta = 359^\circ$. The computed torsional frequencies are compared with the observed infrared frequencies in Table I. The potential function and lower energy levels are plotted in Figure 2.

Table I. Amino Torsional Transitions for Methylhydrazine

Transition	$\nu(\text{calcd})$	$\nu(\text{obsd})^a$
Inner Rotamer		
0 \rightarrow 1	315.0 ^b	315.5 ^c
1 \rightarrow 2	290.2	289
2 \rightarrow 3	258.5	(257) ^d
3 \rightarrow 4	190.0	193 [*]
Outer Rotamer		
0 \rightarrow 1	257.3	257 [*]
1 \rightarrow 2	221.4	222 [*]
2 \rightarrow 3	171.5	
Zero Point Energies (Calcd)		
	$E_1^0 = 163.5 \text{ cm}^{-1}$	
	$E_0^0 = 137.2 \text{ cm}^{-1}$	

^a Frequencies marked with an asterisk (*) have been reassigned from the spectrum of Durig, *et al.*¹⁰ ^b All frequencies in cm^{-1} . ^c Reported accuracy is $\pm 2 \text{ cm}^{-1}$. ^d Masked by a stronger transition, $\nu_0(0 \rightarrow 1)$.

Reevaluation of the Far-Infrared Spectrum

Normal Isotopic Species. While making our calculations, we found it necessary to reevaluate the far-infrared torsional spectrum of methylhydrazine in order to arrive at reasonable conclusions concerning the shape of the torsional barrier and the positions of the energy levels. This involved, first of all, the assignment of observed infrared lines to outer rotamer transitions, since Durig, *et al.*,¹⁰ had interpreted the spectrum solely on the basis of one rotamer being present. The 257-cm^{-1} line was assigned to the outer torsion fundamental primarily on the basis of its intensity. In the observed spectrum three lines clearly stand out as being stronger than the others. Two of three lines, at 315.5 and 289 cm^{-1} , are unambiguously assignable to the $0 \rightarrow 1$ and

$1 \rightarrow 2$ inner transitions. The outer fundamental is expected to be of comparable intensity to the inner $1 \rightarrow 2$, since the ground state of the outer well lies $\sim 20 \text{ cm}^{-1}$ lower than the first-excited inner energy level. On this basis then, the outer fundamental was assigned to the frequency of the third strong line, at 257 cm^{-1} . It should be noted that the $2 \rightarrow 3$ inner transition also falls near the 257-cm^{-1} frequency, but this transition should be considerably weaker than the observed intensity of the 257-cm^{-1} transition. The assignment of the 257-cm^{-1} line to the outer fundamental is satisfying in that it leads to a reasonable assignment of the outer $1 \rightarrow 2$ transition to the observed 222-cm^{-1} line and of the $\text{CH}_3\text{-ND-ND}_2$ line at 187 cm^{-1} to the outer fundamental of the N-deuterated molecule. (The $\text{CH}_3\text{-ND-ND}_2$ molecule is discussed more fully in a later section.)

Our reassignment of amino torsional frequencies also led us to a reevaluation of the methyl torsional mode in methylhydrazine, since the infrared spectrum shows the hot bands of the two torsions to be overlapped. A question immediately arose as to the assignment of the methyl fundamental, which Durig, *et al.*,¹⁰ placed at 257 cm^{-1} , the same value as the newly assigned outer amino fundamental. We suggest a reassignment of the weak band at 262 cm^{-1} to the methyl fundamental. The 262-cm^{-1} band seems more consistent for two reasons: First, its intensity is more in line with what one might expect (*i.e.*, the methyl frequencies are expected to be weaker than the amino frequencies); and second, the 262-cm^{-1} line is more in line with the microwave value of the threefold barrier (1329 cm^{-1}), which predicts the methyl fundamental to lie at 261.3 cm^{-1} . With this reassignment of the methyl fundamental, the observable methyl hot bands have also been reassigned (Table II). A least-squares fit gives a threefold barrier of 1338 cm^{-1} using this new assignment.

Table II. Methyl Torsional Transitions for Methylhydrazine

Transition	$\nu_A(\text{calcd})$	$\nu_B(\text{calcd})$	$\nu(\text{obsd})^a$
0 \rightarrow 1	262.1 ^b	262.1	262 [*] ^c
1 \rightarrow 2	245.5	245.5	248 [*]
2 \rightarrow 3	226.9	226.4	225
3 \rightarrow 4	200.6	205.3	202
4 \rightarrow 5	194.7	162.0	(193) ^d
	$F = 6.389 \text{ cm}^{-1}$		
	$s = 93.08$		

^a Frequencies marked with an asterisk (*) have been reassigned from the spectrum of Durig, *et al.*¹⁰ ^b All frequencies in cm^{-1} . ^c Reported accuracy is $\pm 2 \text{ cm}^{-1}$. ^d Also assigned to $\nu_1(3 \rightarrow 4)$, see Table I.

The methyl torsional bands discussed here are best attributed to the inner skew rotamer. Transitions originating from the outer rotamer would be only about one-fifth as intense because of the lower abundance and would escape detection easily. It is possible also that the CH_3 torsional barriers are rather similar for the two rotamers, which would lead to coincident bands. Since the CH_3 torsional satellites of the outer rotamer were not identified in the microwave study,¹¹ it has not been possible to determine the barrier and torsional frequency for this rotamer.

N-Deuterated Species. One test that was performed to test the results was the prediction of the amino

torsional transitions for the $\text{CH}_3\text{-ND-ND}_2$ molecule, which were observed and measured by Durig, *et al.*¹⁰ The potential function was assumed not to vary in going to the N-deuterated species, and thus the only change made in the Hamiltonian was in the reduced moment I_r . This parameter was varied until a reasonable agreement was obtained with the observed spectrum. The value of $(I_r)_0$ determined by this method was $3.20 \text{ amu } \text{Å}^2$ ($F_0 = 5.27 \text{ cm}^{-1}$). To serve as a check on this value, I_r was determined using the method described previously for the undeuterated molecule. This gives $(I_r)_0 = 3.00 \text{ amu } \text{Å}^2$ ($F_0 = 5.61 \text{ cm}^{-1}$), which is reasonably close to the value which is obtained by using I_r as a variable. Using $(I_r)_0 = 3.20 \text{ amu } \text{Å}^2$, the computed infrared frequencies (Table III) fit the measured frequencies with

Table III. Amino Torsional Transitions for Methylhydrazine ($\text{CH}_3\text{-ND-ND}_2$)

Transition	$\nu(\text{calcd})$	$\nu(\text{obsd})^a$
Inner Rotamer		
0 \rightarrow 1	228.9 ^b	231 ^c
1 \rightarrow 2	217.3	216
2 \rightarrow 3	204.1	200
3 \rightarrow 4	188.4	(187) ^d
4 \rightarrow 5	167.5	164
Outer Rotamer		
0 \rightarrow 1	189.5	187*
1 \rightarrow 2	173.5	172*
2 \rightarrow 3	153.7	158*
Zero Point Energies (Calcd)		
	$E_0^0 = 117.4 \text{ cm}^{-1}$	
	$E_0^0 = 98.8 \text{ cm}^{-1}$	

^a Frequencies marked with an asterisk (*) have been reassigned from the spectrum of Durig, *et al.*¹⁰ ^b All frequencies in cm^{-1} . ^c Reported accuracy is $\pm 2 \text{ cm}^{-1}$. ^d Masked by a stronger transition, $\nu_0(0 \rightarrow 1)$.

an average deviation of less than $\pm 3 \text{ cm}^{-1}$. This agreement is reasonable but not as good as for the undeuterated species. The agreement with expected intensities is good, however, and the assignment of the relatively strong 187-cm^{-1} transition to the outer fundamental provides a check on the outer fundamental assignment for the undeuterated molecule. It should be stressed that we have fit seven far infrared transitions to only one variable, $(I_r)_0$, and a predetermined set of Fourier coefficients.

Discussion of Results

The consistency of the results with experimental measurements is reasonably good, considering (1) that the observed far-infrared frequencies are very much bunched together and hence difficult to separate and assign unambiguously, and (2) that there is some degree of uncertainty in the microwave values, particularly θ_1 and θ_0 . The observed far-infrared transitions are rather sensitive to small changes in the trans barrier, and it is believed that this barrier has been determined to $\sim 2\%$ accuracy, or about $\pm 25 \text{ cm}^{-1}$. The energy levels near the top of this barrier are extremely sensitive to the barrier height. These levels are only sparsely populated, however, and transitions arising from them are not clearly observable and assignable from the far-infrared spectrum of Durig, *et al.*¹⁰ For this reason Table I lists only the lower transitions for which an assign-

ment can be made with some confidence. The cis barrier is considerably less well determined by the present study, since this higher barrier is so far removed from the observable energy levels. The cis barrier accuracy may only be $\sim 10\%$, or $\pm 300 \text{ cm}^{-1}$.

Qualitatively, the potential function looks very reasonable. The cis barrier, as expected, is very high due to the lone pair-lone pair repulsion of the two nitrogen atoms. The trans position shows no minimum, in agreement with the theoretical studies of hydrazine.^{4-6,12} It is interesting to note that the theoretical values of N_2H_4 computed by Fink, *et al.*,⁵ namely $V_c = 11.9 \text{ kcal/mol}$ and $V_t = 3.70 \text{ kcal/mol}$, are in reasonably good agreement with our results for methylhydrazine. If the dominant barrier contributions are from the nitrogen lone pair electrons, this agreement is reasonable. With regard to the relative stabilities of the inner and outer rotamers of methylhydrazine, Radom, *et al.*,⁷ have recently published theoretical results which indicate that the inner rotamer is less stable than the outer by 0.11 kcal/mol . While this result is qualitatively in agreement with previous assumptions concerning the conformations of the molecule,^{10,23} it disagrees with the microwave results¹¹ upon which the present study is based. The absolute discrepancy is less than 1 kcal/mol and is probably not surprising in view of the relatively simple nature of the molecular orbital computations.⁷

Entropy Considerations

The difference in the experimental entropy (from heat capacity measurements) and the calculated entropy (from spectroscopic data) has been used as a criterion for estimating the entropy of mixing of the inner and outer rotamers of methylhydrazine.^{10,23} Such considerations have led to an estimation that $\sim 91\%$ of methylhydrazine molecules at 25° are in the most abundant rotameric form.²⁴ The actual percentage, as determined in the present study by evaluating the partition functions of the localized eigenstates, is found to be only 78.4% inner rotamer. In the light of this inconsistency, it seemed appropriate to reconsider the entropy question. A summary of our spectroscopic entropy calculations is presented in Table IV. S_{rot} is based on

Table IV. Entropy Calculations for Methylhydrazine

Spectroscopic Entropy, eu	
$S_{\text{tr}} = 37.409$	$S_{\text{mix}}^* = 1.038$
$S_{\text{rot}} = 22.179$	$S_{\text{Me}} = 1.782$
$S_{\text{vib}} = 1.648$	$S_{\text{NH}_2} = 2.617$
$S_{\text{mix}}^0 = 1.377$	$S_{\text{total}} = 68.050$
Heat Capacity Entropy, ²³ eu	
	$S' = 66.61 \pm 0.20$
	$S_{\text{total}} - S' = 1.44$

the microwave rotational constants and has been corrected for the difference in rotational constants between the inner and outer rotamers. S_{vib} is calculated from the infrared gaseous frequencies¹⁰ of 19 fundamentals (excluding the torsions). The torsional entropies (S_{Me}

(23) J. G. Aston, H. L. Fink, G. J. Janz, and K. E. Russell, *J. Amer. Chem. Soc.*, **73**, 1939 (1951).

(24) It was earlier incorrectly assumed (ref 10 and 23) that the outer rotamer was the most stable one. This error does not appreciably influence the entropy calculations.

and S_{NH_2}) were calculated by evaluating the partition functions from the eigenstates determined in this study. S_{mix}^r is based on 78.4% inner and 21.6% outer rotamers.

It is seen that the spectroscopic entropy is 1.44 eu greater than the heat capacity value. This excess may be interpreted as evidence for residual entropy in methylhydrazine at 0°K. In particular, if it is assumed that $S_{\text{mix}}^o (= R \ln 2)$, the entropy of mixing of optical isomers, is present at 0°K, then the spectroscopic entropy agrees with the heat capacity value to within experimental error.

Conclusion

In this paper we have utilized an approximate quantum mechanical method to determine the shape of the barrier hindering the torsion about the N-N bond in methylhydrazine. We have determined the first six Fourier coefficients which may be used to describe this barrier and have presented a reasonable explanation for the far-infrared torsional spectrum of the molecule.

Using our barrier description we have reexamined the entropy of methylhydrazine and have found our results to be consistent with the entropy determined experimentally from heat capacity measurements.

Currently in our laboratory we are reexamining the torsional barrier in the parent hydrazine molecule. Kasuya¹⁶ attempted to determine this barrier, but the model used was an incorrect one which assumed the cis and trans barriers to be equal. We are attempting to obtain a more satisfactory barrier description by (1) utilizing additional Fourier terms in the potential energy expression for the barrier, and (2) combining the results of the microwave¹⁶ and far infrared²⁵ studies of the molecule.

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(25) A. Yamaguchi, I. Ichishima, T. Shimanouchi, and S. Mizushima, *Spectrochim. Acta*, **16**, 1471 (1966).

Relaxation Amplitudes for Systems of Two Coupled Equilibria

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Abstract: Equations are developed allowing one to set down, merely by inspection of the stoichiometry, the relation between the overall change in signal following the perturbation of a system of two coupled equilibria and the thermodynamic functions associated with the elementary steps. It is shown that expressions for individual relaxation amplitudes can also be calculated by inspection. The treatment includes the case where a strong kinetic coupling exists between the two equilibria. Applications are cited involving the determination of enthalpies for the fixation of the competitive inhibitors proflavin and benzamidine to trypsin.

In transient chemical relaxation techniques a reaction solution at equilibrium is perturbed by a rapid change in some external variable, such as temperature or pressure.¹ If the perturbation is sufficiently small, the time dependence of the reactant concentrations is characterized by a series of exponential decays. Relaxation amplitudes, or the net signal changes associated with the observed exponentials, are measures of equilibrium shifts and can be used to determine thermodynamic functions (ΔH , ΔV , etc.) for elementary reaction steps. Amplitudes are also related to the question of whether a relaxation process is observable and can serve as a check on a mechanism suggested by kinetic information.

The general thermodynamic relations governing chemical relaxation have been developed by Eigen and DeMaeyer,¹ who discuss a "normal mode" analysis

(1) M. Eigen and L. DeMaeyer, "Techniques of Organic Chemistry," Vol. VIII, 2nd ed, Part 2, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Wiley, New York, N. Y., 1963, p 895.

(2) G. H. Czerlinski, "Chemical Relaxation," Marcel Dekker, New York, N. Y., 1966.

of relaxation amplitudes. Czerlinski,² in a different approach, has derived amplitude expressions for quite a number of mechanisms in which the elementary steps equilibrate at very different rates.

For multistep mechanisms the equations relating thermodynamic parameters and relaxation amplitudes are often numerically complex, and their derivations can be tedious. In the present paper such relations are considered for systems of two coupled equilibria. Equations are developed allowing one to set down, merely by inspection of the stoichiometry, the relation between the *overall* change in signal induced by a physical perturbation, and the thermodynamic parameters associated with the elementary steps. It is shown that expressions for *individual* relaxation amplitudes can also be calculated by inspection. The treatment includes the case where a strong kinetic coupling exists between the two equilibria. Practical applications are cited involving the determination of enthalpies for the fixation of the competitive inhibitors proflavin and benzamidine to trypsin.