



Microwave Spectrum of NMethyl Methylenimine

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and is consistent also with the intuitive idea that the correlation should not be of shorter range than the potential.

It should be made clear what the logical position of Eq. (22) is. The quantity $\omega(K)$ in Eq. (18) is the Fourier transform of the direct correlation function which, in turn, as is frequently remarked, is known only from its definition in terms of G(r) but has no independent physical meaning. Thus, the assumptions which are made about $\omega(K)$ in deriving Eq. (20) in the Ornstein-Zernike theory are exactly equivalent to having assumed the truth of Eq. (20) in the first

place. At the moment, precisely the same is the case with Eq. (22). The assumptions made about $\Omega(\mathbf{K})$, however innocent in appearance, amount to having assumed Eq. (22) in the first place. However, unlike $\omega(K)$, the new quantity $\Omega(\mathbf{K})$ does have a physical meaning independent of G(r) itself, and this is in Eq. (15) which relates $\Omega(\mathbf{K})$ to the spatial variation of the local reciprocal activity coefficient $\exp[-\Psi(\mathbf{r})/kT]$. There is then a chance, which is perhaps not too remote, that the properties of G(r) may ultimately be derived by a noncircular argument from an independent study of the properties of $\exp[-\Psi(\mathbf{r})/kT]$.

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Microwave Spectrum of N-Methyl Methylenimine*

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The rotational spectrum of CH₃NCH₂ has been studied in the region 7000–49 000 Mc/sec. Several *b*-type transitions have been identified. The barrier to the internal rotation of the methyl group has been found to be 1970 ± 25 cal/mole. Quadrupole fine structure components for several transitions have been analyzed. The components of the quadrupole tensor χ_{ee} and χ_{ae} have been found to be 3.2 ± 0.2 and 1.9 ± 0.3 Mc/sec, respectively. The electric dipole moment has been found to be 1.53 ± 0.020 D by measurement of Stark effects.

INTRODUCTION

THE investigation of the rotational spectrum of *N*methyl methylenimine has been carried out with a view to studying the barrier to the internal rotation of the methyl group in molecules containing the $CH_3-N=$ group. The microwave spectrum of a similar molecule methyl isocyanate was investigated earlier¹ in this laboratory and found to have a very low barrier to the internal rotation.

EXPERIMENTAL

N-methyl methylenimine was prepared² by the sequence of reactions



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[†] Alfred P. Sloan Foundation Fellow. ¹ R. F. Curl, V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, J. Chem. Phys. **39**, 3335 (1963).

² J. L. Anderson, U.S. Patent 2,729,679 (January 1956).

The trimer 1,3,5-trimethylhexahydrosymtriazine was prepared by mixing equal quantities of 33% methylamine in water and 40% formaldehyde in water at 0°C. The trimer separates as an oily liquid on adding KOH. It is further dried by treating with solid KOH. CH₃NCH₂ was prepared by dripping the trimer onto a bed of fused alumina and SiO₂ packed into a **U**-tube and maintained at 425°-450°C. The hot bed was continuously pumped. The products were collected in a liquid-nitrogen trap. CH₃NCH₂ was distilled from the trap into a storage container under vacuum and also stored at liquid N₂ temperature. After each preparation, the SiO₂, Al₂O₃ bed was covered with char. On subsequent preparations, a clean SiO₂, Al₂O₃ bed was required to obtain a good yield.

The spectrum was observed at dry-ice temperature using a conventional 100-kc/sec Stark modulation spectrograph. The microwave power in the frequency region, 37 000 to 49 000 Mc/sec, was obtained using a frequency doubler. A varactor diode (RCA GaAs Type VD-215) was used as the nonlinear element.

OBSERVED SPECTRUM

The observed spectrum consists of well-separated doublets. These doublets were found to arise from internal rotation splittings. The first four Q-branch b-type transitions $(J_{0,J} \rightarrow J_{1,J-1})$ were identified by their Stark effects. These transitions occur as two series with identical Stark effects and quadrupole structure. One series corresponds to nondegenerate levels of symmetry A, and the other corresponds to the

Rotational transition	Hyperfine transition $F \rightarrow F'$	$\begin{array}{c}A\\\nu_{\rm obs}\\({\rm Mc/sec})\end{array}$	E (Mc/sec)	$\begin{array}{c}A\\\nu_{0 \text{obs}}\\(\text{Mc/sec})\end{array}$	$\begin{array}{c} A \\ \nu_{00alo} \\ (Mc/sec) \end{array}$	
1 ₀₁ -1 ₁₀	2-2 2-1 1-0	43 148.98 43 149.72 43 146.80	43 130.8 43 129.0	43 148.91	43 146.56	
2 ₀₂ -2 ₁₁	33 2-2	44 466.7 44 468.1	44 447.2 44 448.6	44 467.25	44 464.82	
3 ₀₃ -3 ₁₂	4-4 3-3	46 498.7 46 500.3	46 478.5 46 480.3	46 499.28	46 496.86	
4 ₀₄ -4 ₁₃ ª	5–5 4–4	49 308.5 49 310.0	49 288.6 49 290.6	49 309.25	49 307.07	
212-303	1-2 2-3 3-4	19 410.70 19 412.95 19 411.40	19 429.67 19 431.98 19 430.48	19 411.78	19 414.83	
3 ₁₃ -4 ₀₄	$2-3^{b}$ $4-5^{b}$ 3-4	41 112.92 41 114.44	41 131.00 41 132.37	41 113.35	41 117.48	
5 ₁₆ -4 ₂₂ ª	$\left. \begin{array}{c} 4-3^{\mathrm{b}} \\ 6-5^{\mathrm{b}} \\ 5-4 \end{array} \right\}$	37 568.6 37 570.4	37 524.4 37 526.0	37 569.50	37 572.09	
6 ₁₆ -5 ₂₃ ª	$\begin{array}{c} 7-6^{\mathrm{b}}\\ 5-4^{\mathrm{b}}\\ 6-5\end{array}$	22 133.3 22 135.2	22 085.2 22 086.6	22 134.25	22 135.19	
4 ₁₃ -3 ₂₂	5-4 3-2 4-3	$\begin{array}{c} 40 & 964.48 \\ 40 & 964.88 \\ 40 & 962.70 \end{array}$	40 896.08 ^b 40 894.10	40 963.98	40 966.68	
5 ₁₄ 4 ₂₃	6-5 5-4 4-3	17 811.40 17 809.70 17 811.60	17 756.00 17 754.20 17 756.26	17 810.88	17 810.86	
7 ₁₇ -6 ₂₄	87 65 76	7839.5 ^b 7841.55	7790.01 7789.79 7791.90	7840.20	7839.84	
11 _{2,9} -12 _{1,12} °	11-12 12-13b)	40 692.6	40 742.2	40 694.59	40 686.59	
	10–11 ^b	40 695.6	40 745.2			

TABLE I. Assigned transitions of CH₃NCH₂.

^a These lines are omitted in the quadrupole hyperfine structure analysis. For these lines the number listed as ν_0 is the average of the component frequencies not the hypothetical rotor frequency.

^b These hyperfine components are not resolved.

^c This line was omitted in the rotational constant fitting.

doubly degenerate levels of symmetry E. From the magnitude of the splitting between the series, it was clear that the barrier to internal rotation was high. The constants (A-C)/2 and κ were obtained by fitting these lines. The remaining rotational constant could be then obtained approximately by using the relationship between the moments of inertia which exists when a molecule is planar except for a methyl group. The spectrum was predicted using the resulting rotational constant. Eight more lines were then identified for each internal rotation series with the help of the predicted frequencies and Stark effects. Only b-type transitions were observed. All the observed lines showed either resolved or partially resolved quadrupole hyperfine structure due to the nitrogen nucleus. The splittings of quadrupole hyperfine structure components and their intensities were studied by tracing each line on a recorder. Table I gives the frequencies of the assigned lines.

TABLE II.	Rotation	al constant	s of A	lines.ª
	= 52 523.7	$75 \pm 1.2 \text{ M}_{\odot}$	c/sec	

 $B = 10 \ 666.13 \pm 0.3$ $C = 9 \ 377.19 \pm 0.3$ $S = 2.9 \ Mc/sec$ Moments of inertiab $I_a = 9.6248$ $I_b = 47.3959$ $I_c = 53.9107$ $I_a + I_b - I_c = I_a - \Delta = 3.1100$ Quadrupole coupling constants $\chi_{aa} = 1.9 \pm 0.3 \ Mc/sec$ $\chi_{bb} = -5.1 \pm 0.2$ $\chi_{ac} = 3.2 \pm 0.2$

* Rigid rotor fit of A lines.

^b In amu \hat{A} with the conversion constant 5.05531×10⁵ (amu \hat{A} Mc/sec) used.

Assumed

Methyl group tetrahedral and symmetric about C-N bond. r(C-H) = 1.089 Å $r(C-N) = 1.44^{a}$

Methylene groupb

```
inner hydrogen <CCH=120.5°
               r(CH) = 1.091 \text{ Å}
outer hydrogen <CCH=121.5°
                r(CH) = 1.081 \text{ Å}
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Found

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r(C=N) = 1.30 \text{ Å}
 <CNC = 116.9°
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^a A shortening of the C-N bond of 0.03 Å by hybridization change from sp^3 to sp^2 is assumed. ^b From the structure of propylene found by Lide and Christensen, Ref. 10.

ROTATIONAL CONSTANTS

Rotational constants were obtained by least-square fitting the A-series lines with rotational constants neglecting centrifugal distortion. In this fitting the frequencies in the absence of quadrupole structure ν_0 (obtained after the quadrupole analysis) were used. The frequencies ν_{obs}^{A} and ν_{calo}^{A} are given in Table I. Rotational constants are given in Table II. In addition, the estimated standard deviation S is given in Table II { $S = [\Sigma(\text{obs}-\text{calc})^2/(n_{\text{obs}}-n_{\text{par}})]^{\frac{1}{2}} n_{\text{par}} =$ number of adjustable parameters}.

STRUCTURE

Since the present data on the rotational constants are not sufficient to determine all the structural parameters, the structure of the methyl group, the C-N distance, and the HCH angle and C-H distances on methylene were assumed. The distance C=N and the \angle CNC were calculated from the observed rotational constants. Table III gives the assumed and calculated structural parameters.

TABLE IV. Internal rotation fitting.

Transition	$(\nu_A - \nu_E)_{obs}$ Mc/sec	$(\nu_A - \nu_E)_{calo}$ Mc/sec
1 ₀₁ →1 ₁₀	18.0	19.4
$2_{02} \rightarrow 2_{11}$	19.5	19.7
$3_{03} \rightarrow 3_{12}$	20.2	20.1
$4_{04} \rightarrow 4_{13}$	19.7	20.4
$2_{12} \rightarrow 3_{03}$	-19.0	-18.3
$3_{13} \rightarrow 4_{04}$	-18.0	-17.5
$5_{15} \rightarrow 4_{22}$	44.3	43.2
$6_{16} \rightarrow 5_{23}$	48.3	47.4
$4_{13} \rightarrow 3_{22}$	68.4	69.5
$5_{14} \rightarrow 4_{23}$	55.4	55.3
$7_{17} \rightarrow 6_{24}$	49.6	48.9
$11_{29} \rightarrow 12_{1,12}$	-49.6	-49.6

TABLE V. Internal rotation parameters.

$s = 42.3 \pm 0.19$	$V_3 = 1970 \pm 25^{\circ} \text{cal/mole}$
$\lambda_a = 0.867 \pm 0.01$	
$I_{\alpha} = 3.1635 \pm 0.05$	amu · Å ²
F = 217 031. Mc/s	ec

^a The uncertainty in V_3 arises primarily from the uncertainty in I_{α} .

INTERNAL ROTATION

The method of Kilb, Lin, and Wilson³ was used in calculating the barrier. For the lines with both $K_{-1} < 2$ the term in \mathcal{O}^2 (\mathcal{O} defined by Herschbach⁴) appeared to be sufficient to describe the behavior of the internal rotation splittings. However, for the transitions with $K_{-1}=2$, it has been found necessary to include the terms in \mathcal{P} , \mathcal{P}^3 , and \mathcal{P}^4 . Attempts to use only the \mathcal{P}^2 terms and the elements of P, P³ which connect asymmetry doublets gave $\Sigma(\nu_{obs} - \nu_{calc})^2$ a factor of ten larger than the method described below and a different barrier and λ_a . A computer program was written to vary the value of s (reduced barrier to the internal rotation) and λ_a (the cosine of the angle between the a axis and the C-N bond) by a process of iteration, to give the best least-square fit between the observed and calculated splittings $\nu_A - \nu_E$. The terms in the expansion were treated exactly. Table IV gives the observed and calculated $\nu_A - \nu_B$. The perturbation coefficients were obtained from the tables computed by Herschbach.⁴ Constants used in the barrier calculations and the values of barrier and λ_a are given in Table V. The value λ_a which best fits the internal rotation corresponds to an angle of 30° between the top axis and the *a* axis. The structure of Table III gives this angle as 29°.

TABLE VI. Stark effects and dipole moment of CH₃NCH₂.

Transition	М	$(\Delta \nu/E^2)$ obs Mc/sec cm ² /V ²	$(\Delta \nu/E^2)$ calc Mc/sec cm ² /V ²	
1 ₀₁ →1 ₁₀	1	7.5 ×10-6	7.4 ×10-6	
$2_{02} \rightarrow 2_{11}$	1 2	19.1 ×10-6 8.9 ×10-6	19.9 ×10-6 8.5 ×10-6	
$3_{03} \rightarrow 3_{12}$	2 3	2.6×10^{-6} 9.3 × 10^{-6}	2.5 ×10 ^{−6} 8.6 ×10 ^{−6}	
$4_{04} \rightarrow 4_{13}$	3 4	3.8 ×10 ⁻⁶ 7.9 ×10 ⁻⁶	3.9×10^{-6} 8.1×10^{-6}	
3 ₁₂ →3 ₀₃	0 1 2	3.6×10^{-6} 3.1×10^{-6} 1.17×10^{-6}	3.8×10^{-6} 3.1×10^{-6} 1.19×10^{-6}	
$ \mu_a ^2 = -0.002 \pm 0.005 \text{ D}^2 \mu_b ^2 = 2.34 \pm 0.04 \text{ D}^2$				
$\mu = 1.53 \pm 0.02 \text{ D}$				
S = 4.5%				

³ R. W. Kilb, C. C. Lin, and E. B. Wilson, J. Chem. Phys. 26, 1695 (1957) ⁴ D. R. Herschbach, J. Chem. Phys. 27, 1420 (1957).

=

-		CH ₃ NCH ₂	CH ₃ NCO
	r(C=N)	1.30 Å	1.19 Å
	<cnc< td=""><td>117°</td><td>140°</td></cnc<>	117°	140°
	r(C==0)	•••	1.18 Å
	V_3	1970 cal/mole	50 cal/mole

TABLE VII. Comparison of CH₃NCH₂ with CH₈NCO.ª

^a All parameters not listed are assumed the same

DIPOLE MOMENT

Stark measurements were made for the transitions 101-110, 202-211, 303-312, 404-413 and 212-303 to obtain the components of the dipole moment. The components μ_a^2 and μ_b^2 were obtained by least-squaring the observed lobe speeds, $\Delta \nu / E^2$, with weighting to give a constant relative error. The component μ_a^2 was found to be small, and this must be the reason for not observing any *a*-type transitions. Table VI gives the Stark measurement data and the values of the components of the dipole moment.

QUADRUPOLE COUPLING

Components of the quadrupole tensor χ_{cc} and χ_{aa} $[\chi_{ii} = eQ(\partial^2 V / \partial x_i^2)]$ were obtained by fitting the observed splittings by the method of least squares. The line position in the absence of quadrupole structure was introduced as a parameter for each rotational transition. The coupling constants are given in Table II.

DISCUSSION

It is interesting to compare this molecule with others having the group

Both methyl isocyanate and methyl isothiocyanate have been studied.^{1,5} For these molecules, the barrier to internal rotation is very low (50 cal/mole in CN₃NCO and probably about that in methyl isothiocyanate). In CH₃NCH₂ the barrier to internal rotation has been found to be quite high.

Besides comparing the barrier to internal rotation, it is of interest to compare the structures of these molecules. Unfortunately, no complete structural determination of any of these molecules has been made. In Table VII the probable heavy atom structures of methyl isocyanate and N-methyl methylenimine are compared. The structure of CH₃NCH₂ is that of Table III. The structure of methyl isocyanate is consistent with the microwave spectrum and uses the structure of HNCO.6

The expected length of the C=N bond can be obtained by plotting the bond length versus multiple bond character for C-N bonds using the C-N distance of 1.47 Å and the C=N distance of 1.15 Å and paralleling the same plots for C-C bonds. By this method, $r_{C=N}$ is found to be 1.28 Å. This is in good agreement with the C=N bond length probable in CH_3NCH_2 . The C=N bond length in formaldoxime was found to be 1.276 Å by Levine.⁷ The C=N bond length in CH₃NCO appears much shorter. In fact it is closer to a $C \equiv N$.

These observations can be explained by considering the structure H₃C-N=CH₂ to be an accurate representation of the bonding. The barrier to internal rotation (1970 cal/mole) is the same as that in propylene⁸ (1980 cal/mole). The \angle CNC is reasonable. In a number of cases (e.g., SF_4 ⁹) the unshared electron pairs have been considered to exert a stronger repulsive effect than a bond. The \angle CNC in CH₃NCH₂, 117°, is smaller than 124.3°, the \angle CCC in propylene.¹⁰ This is in agreement with the stronger repulsive effect of the unshared pair.

The low barrier, large ∠CNC and short C=N distance in methyl isocyanate may be explained by the resonance:





There is a similar, but not as marked, drop in the barrier in going from propylene (1980 cal/mole) to methyl ketene¹¹ (1200 cal/mole) indicating a possible similar but weaker resonance. This is understandable since a no-bond resonance would be involved.

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⁶ S. Siegel, thesis, Harvard University, 1959. ⁶ L. H. Jones, J. N. Shoolery, R. G. Shulman, and D. M. Yost, J. Chem. Phys. 18, 990L (1950).

⁷ I. Levine, J. Chem. Phys. 38, 2326 (1963).

 ⁸ D. R. Lide and D. E. Mann, J. Chem. Phys. 27, 868 (1957).
 ⁹ W. M. Tolles and W. D. Gwinn, J. Chem. Phys. 36, 1119 (1962).

¹⁰ D. R. Lide and D. Christensen, J. Chem. Phys. 35, 1374 (1961).

¹¹ B. Bak, D. Christensen, J. Christiansen, L. Hansen-Nygaard, and J. Rastrup-Andersen, Spectrochim. Acta 18, 1421 (1962).