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Microwave Determination of the Structure of Pyridine

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2-, 3-, and 4-mono-deutero-pyridine have been prepared and the microwave spectra recorded. For each of the isotopic species 11-12 transitions (Q- and R-branch lines) were localized, a number of which could be identified by their Stark effect. For all three species rotational constants of high precision were calculated. The material so provided in connection with known rotational constants for ordinary pyridine is insufficient for a complete determination of the ten geometrical parameters of the molecule. Seven models with a choice of C-H distances close to the correct value (1.075-1.085 A) were considered one of which was shown to be consistent with electron-diffraction work and current valence theory. In this model $d(N-C(2))=1.340 \pm 0.005$; $d(C(2)-C(3))=1.390\pm 0.005$; $d(C(3)-C(4))=1.400\pm 0.005$ A. The valence angles in the aromatic ring (starting with the C(6)-N-C(2) angle) are: 116° 42'; 124° 00'; 118° 36'; 118° 06'.

I. INTRODUCTION

THE problem of contributing to our knowledge of the configuration of pyridine by means of microwave measurements was simultaneously attacked by two groups of investigators.^{1,2} While two of the present authors (B.B. and J.R.-A.) were unsuccessful in getting satisfactory agreement between the observed and the calculated spectrum, McCulloh and Pollnow² presented a very convincing analysis, partially based on their demonstration of the somewhat unexpected fact that the axis of *least* moment of inertia coincides with the dipole moment vector, the N-C(4) direction. By studies of the Stark effect for an authentic $1\rightarrow 2$ transition this important property of the pyridine molecule was affirmed.³

McCulloh and Pollnow showed that pyridine is planar with a twofold axis of symmetry, and they calculated the principal moments of inertia. However, the magnitude of ten geometrical parameters must be known for a complete description of the geometry of the molecule. Therefore, determinations of the principal moments of inertia of several isotopic species, in addition to those of pyridine itself, must be made. In principle, the seven isotopic molecules derived from pyridine by isotopic substitution of one of the atoms N, C(2), C(3), C(4), H(2), H(3), and H(4) must be investigated. It is the purpose of the present paper to give data for the microwave spectra of the three monodeuterated pyridines. Although not complete, the picture of the pyridine molecule so obtained has so many interesting details, not subject to change as a result of possible exhaustive studies of the microwave spectra of a further number of isotopic pyridines that it seemed worth while to publish the present result.

II. EXPERIMENTAL PART

A. Preparation of Materials

No methods for the preparation of the partially deuterated pyridines can be found in the literature (pyridine- d_5 has recently been prepared⁴). Preparation from the corresponding halogen derivatives may be possible by means of a modified Grignard technique⁵ (although certainly very difficult). The following simple method for conversion of a monohalogenated pyridine into the corresponding monodeutero derivative of high purity was finally found: 0.0085 mole of highly purified 4-chloro-, 3-bromo-, or 2-bromopyridine was dissolved in 25-cc 2n D₂SO₄ (0.05 equivalents) in a 150-cc flask fitted with reflux condenser. 1.31-g Zn dust (0.05 mole) was added and the mixture was kept at 100°C for 100 minutes under exclusion of atmospheric moisture. The amount of (excess) deuterium evolved corresponded very closely to the simultaneous occurrence of the reactions $Zn+D_2SO_4 \rightarrow ZnSO_4+D_2$ and $C_5NH_4X+D_2 \rightarrow$ C5NH4D+DX (X being a halogen atom), i.e. the pyridine is for example not converted to piperidine (which was found to happen in the reaction $C_5NH_4Cl(4)$) +HJ⁵ also investigated by us). After cooling of the reaction mixture the D₂O solution was separated from excess Zn dust by filtering. 10-15 cc of the deuterium oxide was distilled off at room temperature in vacuo into a receiver in which a mixture of dried $HgCl_2$ (5.5 g) and NaCl (1.5 g) had been placed in advance. The resulting salt solution was added to the contents of the distilling flash under vigorous shaking. After cooling to 0°C the white precipitate formed was filtered off, washed twice with ice-cooled alcohol and three times with dry ether and finally dried in vacuo over conc. H_2SO_4 . The corresponding pyridine complex has first been described by Ladenburg⁶ and its formula proved to be Py, HCl, 2HgCl₂ (m.p. 179°).

In preliminary experiments with pyridine we found that the complex formed by us had the correct melting point but only approximately the composition given by

¹B. Bak and J. Rastrup-Andersen, J. Chem. Phys. 21, 1305 (1953).

²K. E. McCulloh and G. F. Pollnow, J. Chem. Phys. 21, 2082(L) (1953); 22, 681 (1954).

⁸ Bak, Hansen, and Rastrup-Andersen, J. Chem. Phys. 22, 565 (1954).

⁴ Corrsin, Fax, and Lord, J. Chem. Phys. 21, 1170 (1953).

M. Proost and J. P. Wibaut, Rec. trav. chim. 59, 971 (1940).
 A. Ladenburg, Ann. Chem. Justus Liebigs 247, 1 (1888).

TABLE I. Yields of D-pyridines from 0.0085-mole halopyridine and their main infrared absorption lines in the 670-1300 cm⁻¹ region (NaCl optics, Beckmann I.R.2 spectrophotometer). The strongest lines are in italics.

Compound	Ladenb. complex	D-pyridine	Infrared absorption places
2D-pyridine	4.35 g	0.40 g	749, 816, 903, 995, 1031, 1062, 1113, 1154, 1214, 1300
3D-pyridine	3.25-	0.35-	718, 747, 824, 849, 938, 979, 1034, 1087, 1109, 1128, 1198, 1272
4D-pyridine	4.50-	0.50-	709, 743, <i>864</i> , 991, <i>1016</i> , 1071, 1088, 1120, 1218, 1280
Pyridine			<i>703, 749, 9</i> 91, 1031, 1069, 1149, 1217
Pyridine-d5			762, 798, 823, 833, 886, 908, 963, 1011, 1043, 1143, 1228, 1302

TABLE II. Observed and calculated microwave absorption frequencies of mono deutero pyridines in the 18 000-27 000 MHz region.

	2D-pyridine		3D-py	ridine	4D-pyridine	
Transition	Observed	Calcul.	Observed	Calcul.	Observed	Calcul.
$1_{10} \rightarrow 2_{11}$	19537.4ª	19537.1	19523.6ª	19523.0	19116.5ª	19115.6
$1_{01} \rightarrow 2_{20}$	25989.0	25988.2	25949.0	25948.5	26199.3ª	26200.0
$2_{21} \rightarrow 3_{22}$	25260.5°	25261.1	25238.60	25239.3	24827.80	24827.5
$2_{11} \rightarrow 3_{12}$	26135.70	26136.8	26098.0°	26097.4	26204.2ª	26204.5
2 ₁₂ →3 ₁₈	20019.5°	20020.3	19993.5°	19994.8	19950.7*	19950.8
202→303	20050.4°	20049.2	20022.3°	20022.4	20039.6ª	20039.8
964963	18704.5 ^b	18704.6	18751.5 ^b	18751.2		(15188)
7 44 → 7 48	19631.7 ^b	19631.9	19628.8 ^b	19628.9	18322.2 ^b	18322.2
6 34 → 6 32	19843.5 ^b	19843.3	19828.8 ^b	19828.6	19186.0 ^b	19186.2
$9_{54} \rightarrow 9_{73}$	20160.8 ^b	20160.9	20116.7 ^b	20116.6	21847.6b	21847.0
$10_{64} \rightarrow 10_{82}$	20439.5 ^b	20439.7	20372.0b	20372.5	23734.0b	23734.4
1174→1193	20943.0	20943.1	20838.4	20838.1	26634.1 ^b	26633.6

Lines unambigously identified by their Stark effect.
 Q lines identified by the graphical method.
 Lines identified in spite of the presence of adjacent lines.

Ladenburg. Since, however, for our purpose the complex only acts as a suitable "multiplicator" of the small amount of D-pyridine formed (0.3-0.5 g) we did not care too much for its exact characterization. After the drying the complex was mixed with 2.0-g pulverized NaOH in a 40-cc glass tube which was afterwards evacuated, sealed off, and heated for one hour on a steam bath in order to liberate the deuterated pyridine. After cooling in liquid air the tube was opened and connected to a vacuum line. The D-pyridine formed was distilled off at 10°C yielding a product contaminated with about 5 percent of water judging from the infrared absorption curve of the liquid.

Three further distillations from vessels with 0.5, 0.2, and 0.1-g pulverized NaOH sufficed to remove all the water. The infrared spectra taken served to show that the procedure followed here resulted in the production of pure samples, not contaminated with pyridine, isomeric monodeuterated derivatives, or higher deuterated pyridines. The same conclusion could later be drawn from the microwave spectra. Table I gives numerical data in connection with the preparations.

B. Measurements of Microwave Absorption Frequencies and Identification of the Lines

The microwave spectrograph used was of the ordinary Stark-modulation type with a pen-and-ink recorder. Only rough estimates of the line intensities are possible. The built-in frequency standard was repeatedly calibrated against spectral lines of well-known frequency by recording these lines on the paper with the same tuning rate for the klystron as applied at the pyridine experiments. The frequency standard showed great stability, so that the frequencies measured by us are thought to be good to 0.1 MHz. Wherever possible the identity of the lines was secured by studies of their Stark effect, but it must be mentioned that there are serious limitations to the application of this principle for "large" molecules such as pyridine. At approximately every ten MHz a spectral line is found so that little space (if any) is left for the full "development" of the Stark pattern. For $1 \rightarrow 2$ and $2 \rightarrow 3$ transitions, however, it was often possible to carry through a Stark analysis in spite of the presence of adjacent lines. Most of these low-J, R-branch lines have a comparatively large Stark effect which, in the first place, means that they may be observed at low square-wave field intensity (150 volts/cm) where many of the remaining lines do *not* appear, and secondly, that their Stark components move rather vividly around between possible neighboring lines as a function of the square-wave voltage applied. When two or three of these *R*-branch lines had been identified a good estimate of the asymmetry parameter κ could usually be made. This enabled us to start looking for Q lines which could be picked out between candidates by plotting (A-C)/2as a function of κ . Curves intersecting in a point common to a bunch belong to Q-type transitions. Table II gives the observed and identified lines for the three monodeuterated pyridines together with the calculated values based on the interpretation given. We are

TABLE III. Rotational constants (A,B,C) in MHz, asymmetry parameter (κ), and principal moments of inertia (I_a,I_b,I_c) in amu A² of pyridine and deuterated pyridines together with the quantum defect (Q.D.) of all four species.

	2D-pyridine	3D-pyridine	4D-pyridine	Pyridine
A	5900.80±0.14	5889.12 ± 0.12	6038.90 ± 0.13	6039.13 ± 0.03
В	5558.47 ± 0.14	5554.96 ± 0.16	5419.93 ± 0.13	5804.70 ± 0.03
С	2861.76 ± 0.14	2858.02 ± 0.12	2855.78 ± 0.13	2959.25 ± 0.03
к	0.77471 ± 0.00002	0.77951 ± 0.00004	0.61109 ± 0.00002	0.84777 ± 0.00001
Ia	85.663 ± 0.002	85.833 ± 0.002	83.704 ± 0.002	83.701 ± 0.001
Ib	90.939 ± 0.002	90.996 ± 0.002	93.263 ± 0.002	87.081 ± 0.001
I_c	176.633 ± 0.008	176.864 ± 0.007	177.002 ± 0.008	170.814 ± 0.002
0.D.	0.061 ± 0.012	0.035 ± 0.011	0.035 ± 0.012	0.032 ± 0.004

aware of the disadvantage of not giving a full list of the observed frequencies. Such a list would, however, comprise between 500 and 1000 lines for *each* of the isotopic molecules in the 18 000–30 000 MHz interval investigated.

All observed frequencies were corrected for centrifugal stretching using the constants derived by McCulloh and Pollnow from their observations on pyridine. In principle the constants to be applied for the deuterated pyridines are a trifle different, but since the corrections are small (0.1–1.2 MHz) no significant error is committed by using the pyridine constants.

III. CALCULATION OF THE ROTATIONAL CONSTANTS

The rotational constants of the various deuterated pyridines were calculated by first reading (A-C)/2 and κ from the plot of the Q-type transitions. With 2D-pyridine as an example we found that intersection of the curves took place between $[(A-C)/2, \kappa] = [1519.58, 0.77462]$ and [1519.50, 0.77475]. Hence we concluded that $(A-C)/2=1519.52\pm0.02$ and $\kappa = 0.77471\pm0.00002$ ("probable" errors). These values



FIG. 1. Showing positions of pyridine atoms in relation to the principal axes of inertia and the center of mass, T(0,0,0), of the entire molecule. Definition of the angles α , β , γ , δ , and ϵ .

were now inserted in the relationships below together with the experimental values of the frequencies (corrected for centrifugal distortion). This gave 6 different values of A+C, given in the column beside the frequency relations.

	A+C
$\nu(1_{10} \rightarrow 2_{11}) = 2(A+C) + (A-C)/2[3\kappa - 1]$	8762.63
$\nu(1_{01} \rightarrow 2_{20}) = 2(A+C) + (A-C)/2[\kappa + 1 + 2(\kappa^2 + 3)^{\frac{1}{2}}]$	8762.95
$\nu(2_{21} \rightarrow 3_{22}) = 3(A+C) + (A-C)/2[3\kappa - 3]$	8762.37
$\nu(2_{11} \rightarrow 3_{12}) = 3(A+C) + (A-C)/2[\kappa+3-2(4\kappa^2-6\kappa+6)^{\frac{1}{2}}]$	8762.18
$\nu(2_{12} \rightarrow 3_{13}) = 3(A+C) + (A-C)/2[\kappa+3-2(\kappa^2+15)^{\frac{1}{2}}]$	8762.29
$\nu(2_{02} \rightarrow 3_{03}) = 3(A+C) + (A-C)/2[3\kappa - 3 + 2(\kappa^2 + 3)^{\frac{1}{2}} - 2(4\kappa^2 + 6\kappa + 6)^{\frac{1}{2}}]$	8762.97
	,

 8762.56 ± 0.23

We concluded from this that $(A+C)/2=4381.28 \pm 0.12$. The known values of (A-C)/2 and (A+C)/2 result in the rotational constants $A = 5900.80 \pm 0.14$ and $C = 2861.76 \pm 0.14$. From the definition of κ as a function of A, B, and C we then calculated $B = 5558.47 \pm 0.14$.

Table III gives the rotational constants for the three monodeuterated species. Since the rotational constant A refers roughly to the N-C(4)-line, the constant Bto a line in the plane of the molecule perpendicular to the A axis and through the center of mass, and C to the principal axis perpendicular to the plane of the molecule, the qualitative significance of the rotational constants is easy to visualize.

IV. CALCULATION OF THE MOLECULAR MODEL

Based on the moments of inertia given in Table III our first task is to calculate the positions of the hydrogens. All coordinates refer to a Cartesian coordinate system (a,b,c) with its origin in the center of mass of pyridine and coinciding with the principal axes of inertia of that molecule. All moments of inertia and masses with a prime refer to monodeuterated molecules, those without to pyridine itself. Defining

$$k = \frac{M'}{M(m_D - m_H)} = 1.00610 \text{ amu}^{-1},$$

where M is the mass of pyridine, we can write:

$$a^{2} = \frac{k}{4(I_{b} - I_{a})} \cdot \left[(I_{c}' - I_{c}) - (I_{a}' - I_{a}) + (I_{b}' - I_{b}) \right] \\ \times \left[(I_{b}' + I_{b}) - (I_{c}' - I_{c}) - (I_{a}' + I_{a}) \right],$$

$$b^{2} = \frac{k}{4(I_{b} - I_{a})} \cdot \left[(I_{c}' - I_{c}) + (I_{a}' - I_{a}) - (I_{b}' - I_{b}) \right] \\ \times \left[(I_{b}' + I_{b}) + (I_{c}' - I_{c}) - (I_{a}' + I_{a}) \right].$$

By insertion we get the results of Table IV.

If we let small letters refer to the coordinates of the hydrogens, capital letters to the coordinates of the ring atoms $(N(A_1,B_1), C(A_i,B_i))$, where i=2, 3, 4, 5, 6), the molecule being placed as shown in Fig. 1, it is easy to

TABLE IV.	Calculated	positions	of the	hydrogen	atoms in
pyridine (a,b)	(A.U.); mo	ments of i	nertia o	f the hydro	ogens (I^H)
and the carbon	n-nitrogen ri	$\log (I^{5C,N})$	(amu A	1 ²).	-

	H(2)	H (3)	H(4)
a	-1.276 ± 0.004	1.205 ± 0.004	2.493 ± 0.004
a ²	1.630 + 0.010	1.453 ± 0.010	6.213 ± 0.020
b	2.056 ± 0.004	2.153 ± 0.004	
b^2	4.225 ± 0.020	4.634 ± 0.020	
I_H		17.86 ± 0.08	
1 5C, N		65.84 ± 0.08	
I_{λ}^{H}		12.48 ± 0.06	
I, 5C, N		74.60 ± 0.06	

TABLE V. Survey of carbon-hydrogen distances (d(C(i) - H)) (A) assumed at the calculation of molecular models I-VII.

d(C(2) - H)	1.075	1.080	1.085	1.075	1.085	1.075	1.085
d(C(3) - H)	1.075	1.080	1.085	1.080	1.080	1.085	1.075
d(C(4) - H)	1.075	1.080	1.085	1.085	1.075	1.085	1.075
Model no.	I	II	III	IV	v	VI	VII

derive that

1

$$m_N A_1^2 + m_C (2A_2^2 + 2A_3^2 + A_4^2) = I_b - I_b^H = I_b^{5C,N}, \quad (1)$$

$$n_C(2B_2^2 + 2B_3^2) = I_a - I_a^H = I_a^{5C,N}, \quad (2)$$

$$m_N A_1 + m_C (2A_2 + 2A_3 + A_4) = -m_H (2a_2 + 2a_3 + a_4), \quad (3)$$

where (3) expresses, that b is an axis through the center of mass.

These three equations contain six unknowns. It is exactly at this point that some experimental material from, say, C412C13NH5 would be useful. However, for lack of such data we have decided to proceed as follows:

Since we know the location of the hydrogens we may draw circles, centered in the hydrogen positions and with radii $(=d_{CH})$ equal to supposed C-H distances. We have considered the possibilities of Table V because preliminary calculations had revealed that taking d_{CH} = 1.07 A gave $d_{\rm CN}$ = 1.29 A, which is certainly too low, while $d_{\rm CH} = 1.09$ A gave $d_{\rm CN} \ge d_{\rm CC} = 1.38$ A, which is also highly improbable. The variation in the C-H distances considered corresponds approximately to the experimental error in the coordinates of the hydrogens. In what follows the middle position of the hydrogen atoms (Table IV) are taken as "mathematical" points, the experimental uncertainty in these coordinates being approximately included in the range of d_{CH} values considered. The experimental error in the right-hand sides of (1), (2), and (3) is of course still taken into account.

Taking for example model I in Table V we have:

$$(B_2 - 2.056)^2 + (A_2 + 1.276)^2 = 1.075^2, \qquad (4)$$

$$(B_3 - 2.153)^2 + (A_3 - 1.205)^2 = 1.075^2,$$
 (5)

$$A_4 = a_4 - 1.075 = 2.493 - 1.075 = 1.418. \tag{6}$$

This is seen to give three additional equations by the aid of which a complete set of the variables $(A_1, A_2, A_3, A_4, B_2, B_3)$ can be obtained. The results are given in Table VI together with the resulting bond distances and bond angles.

V. CONCLUSIONS AND DISCUSSION

Each of the three dominant methods for determination of molecular structure of gases and vapors, the spectroscopic, the electron-interferometric, and the quantum-mechanical calculation procedure contributes to the picture of pyridine that can now be given.

What may be concluded from spectroscopy is included in Table VI. It is noted that irrespective of the choice of C-H distance the two different C-C distances are about equal to the C-C distance in benzene (1.395 A)as found by Raman technique⁷ (1.396-1.401 A) and electron-diffraction experiments⁸ $(1.393 \pm 0.005 \text{ A})$. However, all the valence angles in pyridine deviate distinctly from 120° so that the pure sp^2 -hybridization present in benzene is slightly disturbed.

Electron-diffraction work⁹ gave d(C(2)-C(3)) indistinguishable from $d(C(3)-C(4))=1.39\pm0.02$ A and $d(N-C(2)) = 1.37 \pm 0.03$ A, leaving the question of the magnitude of the valence angles partially unanswered.

We shall now try to see which structural features for pyridine may be predicted by means of the so-called valence-bond method from quantum mechanics, restricting ourselves to statements of comparative character.

TABLE VI. Calculated values of pyridine ring-atom coordinates $(A_1, A_2, A_3, A_4, B_2, B_3)$, carbon-carbon distances (d(C(i) - C(j))), carbon-nitrogen distance (d(N-C(2))), the C(5)-C(4)-C(3) angle α , the C(4)-C(3)-C(2) angle β , the C(2)-N-C(6) angle γ , the C(4)-C(3)-H(3) angle δ , and the N-C(2)-H(2) angle ϵ as functions of assumed C-H distances (A) (models I-VII).

			· · · · · · · · · · · · · · · · · · ·				
	I	II	111	IV	v	VI	VII
$\overline{A_1}$	-1.370	-1.390	-1.412	-1.388	-1.395	-1.396	-1.388
$\overline{A_2}$	-0.713	-0.698	-0.679	-0.701	-0.691	-0.694	-0.699
A_3	0.706	0.703	0.701	0.708	0.699	0.705	0.700
A	1.418	1.413	1.408	1.408	1.418	1.408	1.418
B_2	1.140	1.144	1.150	1.148	1.142	1.152	1.137
B_3	1.201	1.197	1.192	1.194	1.199	1.190	1.204
d(C(2) - C(3))	1.420	1.402	1.381	1.410	1.391	1.400	1.401
d(C(3) - C(4))	1.396	1.392	1.386	1.384	1.398	1.382	1.402
d(N-C(2))	1.316	1.337	1.364	1.338	1.342	1.349	1.329
α	118° 40′	118° 40′	118° 40′	119° 14′	118° 06′	118° 52′	118° 22'
β	118° 12'	118° 30′	118° 55′	118° 31′	118° 36'	119° 01'	118° 04′
Ŷ	120° 06′	117° 40′	114° 58′	118° 12′	116° 42′	117° 18′	117° 34'
δ	121° 40′	121° 38′	121° 39′	122° 13′	121° 07'	122° 00′	121° 10′
e	118° 28′	116° 28′	114° 06'	116° 45′	115° 44′	115° 53'	116° 40′

⁷ B. Stoicheff, J. Chem. Phys. 21, 1410 (1953).
⁸ I. L. Karle, J. Chem. Phys. 20, 65 (1952).
⁹ V. Schomaker and L. Pauling, J. Am. Chem. Soc. 61, 1769 (1939).

Figure 2 gives the eight dominant bond structures for pyridine together with their relative weights x, y, z, and s (2x+3y+2z+s=1). It is seen that the doublebond character (DBC) of the C(3)-C(4) bond is measured by x+y+z, the sum of the weights of the structures in which the bond has been formulated as double. Correspondingly, the DBC of the C(2)-C(3)bond is x+y+z+s. Hence we conclude that the latter bond must be shorter than the former. It is seen that this condition is only obeyed by models such as III, V, and VII in Table VI.

Furthermore we want to compare the DBC of the C-C distance in benzene with the DBC's of the carbon-carbon bonds in pyridine. Since ionic structures may be ignored for benzene, the DBC for the C-C bond must be measured by (x+y)(2x+3y+2z+s)/(2x+3y)=x+y+(2z+s)(x+y)/(2x+3y). Here, we have assumed that the ratio of the weights of a Kekulé and a Dewar bond structure is the same for benzene and for pyridine. Since $x\sim5.5y$, (x+y)/(2x+3y) is close to 0.5, which means that the DBC for the carbon-carbon bond in benzene is measured by $x+y+z+\frac{1}{2}s$. Therefore, the bond length in the benzene ring is predicted to fall approximately halfway between the two different C-C bonds in pyridine. This is only compatible with models like V and VII.

Finally, we shall ask for the DBC of the N-C(2)bond. It is measured by x+y. Now, it is highly probable that $z \sim s$. To the extent to which this is true we see that the decrease in DBC from the C(2)-C(3) bond to the C(3)-C(4) bond is the same as the decrease from C(3)-C(4) to N-C(2). Therefore, the increase in N-C bond length caused by the presence of ionic structures as compared with a pure Kekulé-Dewar pyridine model approximately equals the difference in lengths between the two unequal C-C bonds. From



FIG. 2. Dominant bond structures for pyridine. x, y, z, and s are the weights of the corresponding structures (2x+3y+2z+s = 1).

Table VI we see that this difference is 0.007 and 0.001 A for models V and VII, respectively. The error in these numbers resulting from experiment amounts to about 0.006 A. If we make the reasonable assumption that the bond-order versus bond-distance curves for C-Cand C-N distances are almost parallel as exemplified by $C_2H_6(C-C=1.54)$, $CH_3NH_2(C-N=1.47)$, and $H_2C_2(C \equiv C = 1.21)$, $CH_3CN(C \equiv N = 1.158)$ with a mutual distance at about 0.06 A near the double-bond point, we conclude that the C-N distance in a Kekulé-Dewar pyridine model would have to be 1.335 A. In the "true" pyridine molecule this distance must be about 0.01 A larger (the approximate magnitude of the difference between the two C-C bonds), i.e. 1.345 A. This happens to fit well with the model V which also had the correct C-C distances.

A C-N distance=1.345 A in pyridine is just barely consistent with the electron-diffraction measurements. The result of future studies of the pyridine structure by means of electron-diffraction technique must be awaited with great interest.

To summarize, a model like V can be pointed out which is consistent with the microwave spectrum and valence theory aspects and not inconsistent with earlier electron-diffraction work. The pyridine molecule pictures in Fig. 1 has the relative dimensions of model V.