

# THE NUCLEAR MAGNETIC RESONANCE SPECTRA OF FOUR SPIN SYSTEMS

## III. Proton Resonance Spectra of $\alpha$ , $\beta$ and $\gamma$ Picolines\*

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Received October 31, 1960

### ABSTRACT

The ring proton resonance spectra of  $\alpha$ ,  $\beta$  and  $\gamma$  picolines have been studied at 40 Mc./sec. The spectra which belong to the classes ABCX, ABXY and  $A_2X_2$  respectively have been completely analyzed to determine all the involved parameters.

### 1. INTRODUCTION

THE proton resonance spectra of pyridine and some deuterated and methyl substituted pyridines were studied earlier by Baker<sup>1</sup> and Bernstein and Schneider,<sup>2</sup> at low resolution (about 1 in  $10^7$ ). These spectra were not therefore completely analyzed to obtain the values of all the parameters. Recently Schneider, Bernstein and Pople<sup>3</sup> have studied again the spectra of pyridine and some deuterated pyridines under high resolution (about 1 in  $10^8$ ) and determined all the parameters by an exact analysis.

With a view to obtain accurate values of the chemical shifts and the spin-spin coupling constants involved, we have studied the proton resonance spectra of  $\alpha$ ,  $\beta$  and  $\gamma$  picolines at 40 Mc./sec. under a resolution of about 1 in  $10^8$ . The analyses of these spectra are presented in this paper.

### 2. EXPERIMENTAL

The samples of  $\alpha$ ,  $\beta$  and  $\gamma$  picolines were kindly provided by Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora. Slight traces of other isomers and some absorbed moisture are the probable impurities in the samples.<sup>4</sup> The spectra were obtained on a V-4300 B Varian High

\* This paper is based on part of a thesis submitted by B. D. Nageswara Rao for a Ph.D. Degree of Muslim University, Aligarh.

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Resolution NMR Spectrometer. The general experimental details were given in an earlier publication.<sup>5</sup>

The resonance of methyl protons, which occurs at a higher field than that of the ring protons, does not show any splitting in all the three cases studied indicating that the coupling of the ring protons with the methyl protons is small. The ring proton resonance spectra of  $\alpha$ ,  $\beta$  and  $\gamma$  picolines are reproduced in Figs. 1(a), 3(a) and 5(a) respectively. A comparison of these spectra with the spectra of pyridine and deuterated pyridines obtained by Schneider *et al.* and a measurement of the areas enclosed under different groups of lines show that the spectra fall into the classes ABCX, ABXY and  $A_2X_2$  respectively in the usual notation,<sup>6</sup> A, B, C, etc., referring to the different ring protons in the molecules as shown in Figs. 2, 4 and 6 respectively. The values of the chemical shifts ( $\delta$ ) for different protons in these molecules with reference signals of water, used as an external standard, are given in Table I.

TABLE I

Values of the chemical shifts\* ( $\delta$ ) for the different protons† in  $\alpha$ ,  $\beta$  and  $\gamma$  picolines with reference to the signal from water

$\alpha$ -picoline		$\beta$ -picoline		$\gamma$ -picoline	
Type of proton	$\delta$ in p.p.m. ( $\pm 0.02$ )	Type of proton	$\delta$ in p.p.m. ( $\pm 0.02$ )	Type of proton	$\delta$ in p.p.m. ( $\pm 0.02$ )
A	-1.70	A	-2.22	A	-1.83
B	-1.69	B	-1.97	X	-3.37
C	-2.12	X	-3.33	CH <sub>3</sub>	3.09
X	-3.26	Y	-3.33	..	..
CH <sub>3</sub>	2.81	CH <sub>3</sub>	3.09	..	..

\* The values are all corrected for bulk diamagnetic susceptibility. The susceptibility values were evaluated with the help of Pascal's constants.

† A, B, etc., denote the different protons in  $\alpha$ ,  $\beta$  and  $\gamma$  picolines as shown in Figs. 2, 4 and 6 respectively.

### 3. $\alpha$ -PICOLINE

The zero order eigenfunctions and the corresponding diagonal matrix elements for the ABCX system are given in Table I of I<sup>5</sup>, and the non-vanishing off-diagonal elements are given in equation (2) of I. A complete solution

of the secular equation requires the diagonalization of four  $3 \times 3$  matrices and hence it is not usually possible to obtain expressions for the transition energies in explicit form. The analysis cannot therefore be done in a straightforward manner.

A comparison of the group of lines due to X proton at the lower field (Fig. 1) with that due to the *ortho*-protons in pyridine<sup>3</sup> shows that the multiplet structure of this group remains practically unchanged, and the mutual separations between these lines are also nearly the same. This indicates firstly that the coupling between the *ortho*-protons in pyridine is small (this was actually found to be so by Schneider *et al.*) and secondly that the values of the coupling constants  $J_{AX}$ ,  $J_{BX}$  and  $J_{CX}$  in  $\alpha$ -picoline do not differ much from the corresponding values in pyridine. In view of this and the general observation that the coupling constants are not much sensitive to substitution, it was expected that a calculation of the spectrum on the basis of the corresponding parameters in pyridine\* would be of help for the analysis. These parameters, expressed in cycles per second, are

$$\left. \begin{array}{l} \nu_A - \nu_B = 0 \\ \nu_A - \nu_C = -15 \\ J_{AC} = J_{BC} = 7.5 \\ J_{AB} = 1.6 \\ J_{AX} = 5.5 \\ J_{BX} = 0.9 \\ J_{CX} = 1.9 \end{array} \right\} \quad (1)$$

Though the spectrum, thus calculated, does not fit in with the observed spectrum correctly, a general resemblance between the two was observed, which furnishes an idea about the probable positions of different transitions in the spectrum. It may be easily noted, from the large number of transitions involved, that there are several unresolved lines in the observed spectrum.

Using these calculations as a starting-point an attempt has been made to assign the lines in the observed spectrum to particular transitions, by trial and error. The following points are of considerable help in deciding upon a proper assignment.

As the off-diagonal elements in a matrix are applied adiabatically in the process of diagonalization (a) the trace of the matrix remains the same and (b) the diagonal elements will not cross each other. If we express the

\* The values of the chemical shifts are also chosen to be the same, in the first instance, as methyl substitution is not expected to alter these drastically.

frequency of a transition between states  $m \rightarrow n$  as  $\nu_{mn} = E_n - E_m$ , using the above rules we get the following relations for the ABC transitions.\*

$$\left. \begin{aligned} \nu_{21} + \nu_{31} + \nu_{41} &= \Sigma \nu_A + \Sigma J_{AB} + \frac{1}{2} \Sigma J_{AX} \\ \nu_{95} + \nu_{10,5} + \nu_{11,5} &= \Sigma \nu_A + \Sigma J_{AB} - \frac{1}{2} \Sigma J_{AX} \\ \nu_{15,6} + \nu_{15,7} + \nu_{15,8} &= \Sigma \nu_A - \Sigma J_{AB} + \frac{1}{2} \Sigma J_{AX} \\ \nu_{16,12} + \nu_{16,13} + \nu_{16,14} &= \Sigma \nu_A - \Sigma J_{AB} - \frac{1}{2} \Sigma J_{AX} \end{aligned} \right\} \quad (2)$$

where

$$\left. \begin{aligned} \Sigma \nu_A &= \nu_A + \nu_B + \nu_C \\ \Sigma J_{AB} &= J_{AB} + J_{BC} + J_{AC} \\ \Sigma J_{AX} &= J_{AX} + J_{BX} + J_{CX} \end{aligned} \right\} \quad (3)$$

And for the X transitions we get

$$\left. \begin{aligned} \nu_{51} &= \nu_X + \frac{1}{2} \Sigma J_{AX} \\ \nu_{16,15} &= \nu_X - \frac{1}{2} \Sigma J_{AX} \\ \nu_{92} + \nu_{10,3} + \nu_{11,4} &= 3\nu_X + \frac{1}{2} \Sigma J_{AX} \\ \nu_{12,6} + \nu_{13,7} + \nu_{14,8} &= 3\nu_X - \frac{1}{2} \Sigma J_{AX} \end{aligned} \right\} \quad (4)$$

If the transitions occurring in equations (2) and (4) are assigned to the lines in the observed spectrum,  $\Sigma \nu_A$ ,  $\nu_X$ ,  $\Sigma J_{AB}$  and  $\Sigma J_{AX}$  can easily be obtained, of which  $\Sigma \nu_A$  and  $\nu_X$  depend on the choice of origin in the observed spectrum.†

After the twelve transitions  $\nu_{21}$ ,  $\nu_{31}$ , etc., in equation (2) were assigned, all the energy levels were computed from the assigned frequencies of these transitions. The remaining eighteen transitions in the ABC spectrum were then calculated and checked with the observed frequencies. The intensities of the corresponding transitions in the theoretical spectrum obtained with the parameters in equation (1) are of help in making this comparison. The agreement between the observed and calculated spectra corresponding to these eighteen transitions forms a check on the assignment of the transitions  $\nu_{21}$ ,  $\nu_{31}$ , etc.

\* This type of procedure has been used earlier by Fessenden and Waugh<sup>7</sup> in the analysis of ABC spectra.

† The value of  $\Sigma \nu_A$  can, however, be utilised to find the position of  $\frac{1}{3} \Sigma \nu_A$  in the observed spectrum. This position may then be fixed as a new origin to express all the transition frequencies in the theoretical and experimental spectra.

Once the observed spectrum is satisfactorily accounted for, the problem would then be to deduce the values of the involved parameters from the energy values. As this cannot be carried out by analytical methods, a numerical method was followed. Different sets of values, for all the parameters were chosen, within reasonable range around the corresponding values in pyridine (also noting the values of  $\Sigma J_{AB}$  and  $\Sigma J_{AX}$  which are known) and the resulting energy levels were calculated for all the sets of values. Finally, the set of values which yield energy values close to those corresponding to the above assignment were chosen as the proper set. These values, in cycles per second, are given below:

$$\left. \begin{array}{ll} \nu_A - \nu_B = 0.5 & J_{AB} = 1.0 \\ \nu_B - \nu_C = -17.0 & J_{BC} = 7.4 \\ & J_{AC} = 7.4 \\ & J_{AX} = 4.5 \\ & J_{BX} = 0.6 \\ & J_{CX} = 2.0 \end{array} \right\} \quad (5)$$

It may be noted that the energy values are considerably sensitive to small changes in the values in equation (5), and therefore, it cannot be said that these values represent the best for *all* the eight parameters. Further refinement of these parameters is discouraged by the presence of several

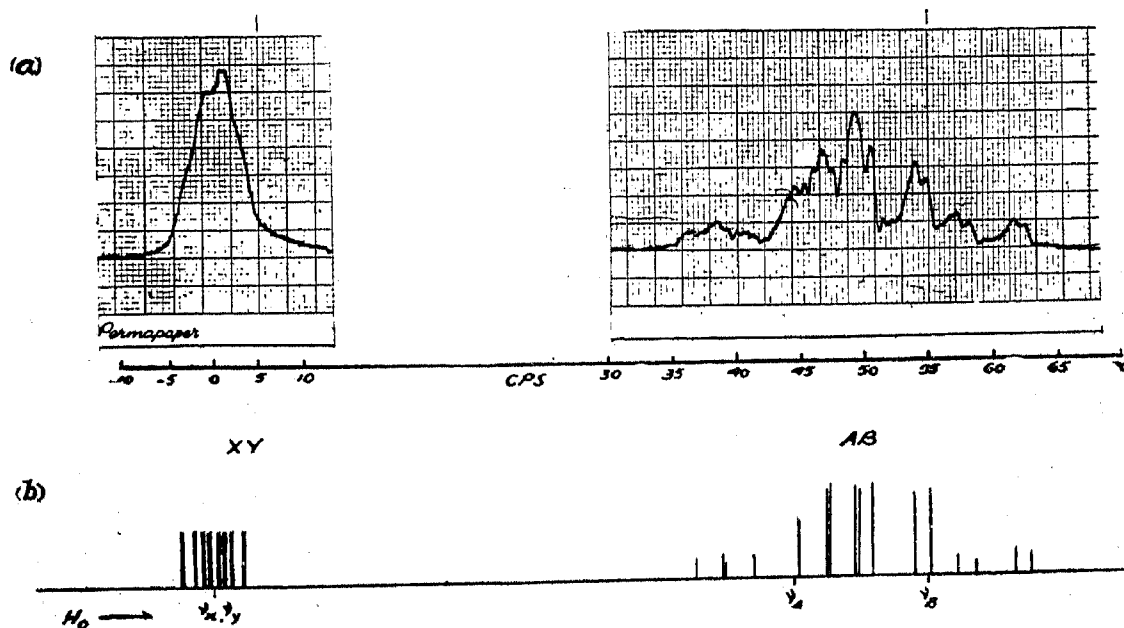


FIG. 1.  $H^1$  NMR spectrum of  $\alpha$ -picoline at 40 Mc./sec. (a) Experimental; (b) Calculated. X spectrum; 1 cm. = 7.636 cps. ABC spectrum; 1 cm. = 4.028 cps.

unresolved lines in the spectrum. The error involved in these values may be about  $\pm 0.5$  cps.

The calculated transition frequencies and relative intensities are given along with the observed frequencies in Table II. The calculated spectrum is shown in Fig. 1 (b).

#### 4. $\beta$ -PICOLINE

The zero order eigenfunctions and the corresponding matrix elements for the ABXY system can be easily obtained from those for the ABCX system (Table I of I<sup>5</sup>) by replacing C and X by X and Y respectively. The non-vanishing off-diagonal elements are given by the following relations:

$$\left. \begin{aligned} H_{25} = H_{7, 11} = H_{8, 10} = H_{12, 15} &= \frac{1}{2} J_{XY} \\ H_{34} = H_{78} = H_{10, 11} = H_{13, 14} &= \frac{1}{2} J_{AB} \end{aligned} \right\} \quad (6)$$

and the remaining elements are given by the condition

$$H_{mn} = H_{nm}$$

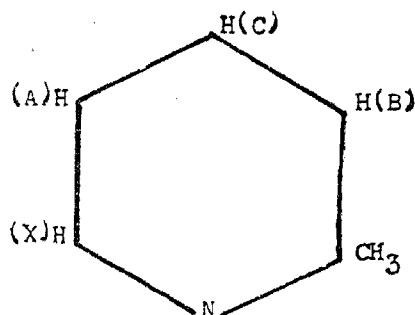


FIG. 2.  $\alpha$ -picoline.

Now the complete spin matrix factors into four  $1 \times 1$  (states 1, 6, 9 and 16), four  $2 \times 2$  (states 2 and 5, 3 and 4, 12 and 15 and 13 and 14) and one  $4 \times 4$  (states 7, 8, 10 and 11) sub-matrices. Explicit expressions, in terms of the parameters involved, can easily be derived, for all but four states, 7, 8, 10 and 11.

The coupling constant in pyridine corresponding to  $J_{XY}$  was found to be 0.4 cps.<sup>3</sup> It can also be seen from the group of lines assigned to X and Y that  $J_{XY}$  should be small. It was therefore assumed that  $J_{XY} = 0$  to carry out the analysis. The validity of this assumption can be judged from the extent to which the analysis on this basis accounts for the observed spectrum. Substituting  $J_{XY} = 0$  the secular equation can be completely

TABLE II

Calculated transition frequencies and relative intensities, and observed frequencies for  $\alpha$ -picoline\*

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
<i>ABC lines</i>				
1	2' → 1	20.8	21.0	0.40
2	9' → 5	18.8	18.9	0.41
3	7' → 3'	16.8	15.3	0.14
4	14' → 11'	14.4		0.37
5	8' → 3'	14.3		0.46
6	7' → 4'	13.2	12.0, 10.9	0.71
7	13' → 11'	11.8		0.49
8	14' → 10'	11.7		0.33
9	8' → 4'	10.7		0.24
10	13' → 10'	9.2		0.21
11	15 → 6'	6.7		6.3
12	16 → 12'	4.7	4.3	2.04
13	4' → 1	1.1	..	0.66
14	6' → 3'	- 0.6	- 1.9, - 3.4§	2.58
15	10' → 5	- 2.0		0.20
16	3' → 1	- 2.5		2.16
17	12' → 11'	- 3.6		2.82
18	6' → 4'	- 4.2		0.69
19	11' → 5	- 4.6		2.37

TABLE II (Contd.)

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
20	12' → 10'	- 6.3	- 6.2	0.22
21	7' → 2'	- 6.6		0.92
22	15 → 8'	- 8.2	- 8.0	0.30
23	8' → 2'	- 9.0		0.48
24	14' → 9'	- 9.1		1.21
25	15 → 7'	-10.7	-10.5, -13.1, -14.8?	0.71
26	16 → 13'	-10.8		0.53
27	13' → 9'	-11.6		0.83
28	16 → 14'	-13.3		0.92
29	6' → 2'	-23.9	...	0.0042
30	12' → 9'	-27.1	...	0.0071
<i>X lines</i>				
1	9' → 3'	24.0	..	0.0009
2	9' → 4'	21.3	..	0.001
3	14' → 6'	16.4	..	0.001
4	13' → 6'	13.9	..	0.002
5	10' → 3'	4.1	4.1	0.38
6	5 → 1	3.6	2.0, 0.5	1.00
7	9' → 2'	1.5		0.99
8	14' → 8'	1.5		0.71
9	11' → 3'	1.5		0.60
10	10' → 4'	0.5		0.49



TABLE II—(Contd.)

Sl. No.	Transition†	Calculated frequency (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
11	14' → 7'	- 0.9	- 1.9	0.30
12	13' → 8'	- 1.0		0.007
13	12' → 6'	- 1.6		1.00
14	11' → 4'	- 2.1		0.52
15	13' → 7'	- 3.5	- 3.5§	0.98
16	16 → 15	- 3.6		0.46
17	12' → 8'	-16.5	..	0.0008
18	12' → 7'	-18.9	..	0.0011
19	10' → 2'	-19.2	..	0.0002
20	11' → 2'	-21.9	..	0.0002

\* The frequencies of ABC transitions are expressed relative to  $\frac{1}{3}(\nu_A + \nu_B + \nu_C)$  as the origin while those of X transitions are expressed relative to  $\nu_X$  as the origin.

† The states involved in the transitions are labelled just as in I.

‡ Average standard deviation for the observed frequency determinations is about  $\pm 0.25$  cps.

§ These lines are observed only as humps. The line at  $-14.8$  cps. does not seem to fit in the analysis of the spectrum.

solved, and explicit expressions may be derived for all the transition energies and relative intensities.

The problem now becomes very much similar to that of 1-fluoro, 2, 4-dinitrobenzene (I). By replacing C and X by X and Y respectively and then substituting  $J_{XY} = 0$  in Tables II (a), II (b) and II (c) of I<sup>5</sup> the transition energies and relative intensities involved in this problem are obtained.

In the present case only the AB part of the spectrum has been analyzed as the X and Y lines (at the lower field in the observed spectrum) are hardly resolved. The theoretical AB spectrum consists of four quartets as in the case of 1-fluoro, 2, 4-dinitrobenzene, and the assignment of the lines to these quartets has been done in a similar manner. From this assignment

the values of  $J_{AB}$ ,  $(\nu_A - \nu_B)$ ,  $(J_{AX} - J_{BX})$  and  $(J_{AY} - J_{BY})$  were obtained. The centres of  $D_+$ ,  $F_+$ ,  $F_-$  and  $D_-$  quartets (see I) in the AB spectrum, with reference to  $\frac{1}{2}(\nu_A + \nu_B)$ , are respectively given by

$$\left. \begin{aligned} &\frac{1}{4} [(J_{AX} + J_{BX}) + (J_{AY} + J_{BY})] \\ &\frac{1}{4} [-(J_{AX} + J_{BX}) + (J_{AY} + J_{BY})] \\ &\frac{1}{4} [(J_{AX} + J_{BX}) - (J_{AY} + J_{BY})] \\ &\frac{1}{4} [-(J_{AX} + J_{BX}) - (J_{AY} + J_{BY})] \end{aligned} \right\} \quad (7)$$

and from these the values of  $(J_{AX} + J_{BX})$  and  $(J_{AY} + J_{BY})$  were obtained. Thus all the parameters except  $(\nu_X - \nu_Y)$  were derived from the analysis of AB spectrum alone. It was, however, not possible to deduce the signs of the coupling constants from the analysis, as was done in the case of 1-fluoro, 2, 4-dinitrobenzene, since no information could be obtained from the X and Y lines. The analysis was therefore carried out assuming all the coupling constants to be positive. The values of the parameters finally obtained are as follows (in cycles per second):

$$\left. \begin{aligned} (\nu_A - \nu_B) &= 10.3 & J_{AB} &= 7.9 \\ & & J_{AX} &= 1.7 \\ & & J_{BX} &= 4.8 \\ & & J_{AY} &= 2.5 \\ & & J_{BY} &= 1.2 \\ & & J_{XY} &= 0 \end{aligned} \right\} \quad (8)$$

The error involved in any of these values is not more than  $\pm 0.4$  cps.

As all the lines of X and Y lie very close within a small region in the observed spectrum,  $(\nu_X - \nu_Y)$  was taken as zero to calculate the spectrum.\* The transition frequencies and relative intensities calculated on the basis of the parameters in equation (8) are given in Table III along with the observed frequencies. The calculated spectrum is shown in Fig. 3 (b). The good agreement between the observed and calculated spectra lends justification to the assumptions made in the analysis.

### 5. $\gamma$ -PICOLINE

The general theory of  $A_2X_2$  type of spectra was given earlier by several authors,<sup>8-10</sup> according to which the spectrum would consist of two groups

\* When  $(\nu_X - \nu_Y) = 0$  and  $J_{XY} = 0$ , the ABXY system may also be called as an ABXX' system.

TABLE III

Calculated transition frequencies and relative intensities, and observed frequencies for  $\beta$ -picoline

Transition No.*	Calculated frequency† (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
<i>AB lines</i>			
2	36.7	36.7	0.36
6	38.9	39.0	0.46
10	39.1		0.30
14	41.3		41.4§
1	44.6	44.7§	1.64
5	46.8	46.7§	1.54
9	47.0		1.70
3	49.1		49.1
13	49.2	1.58	
11	50.5	50.3	1.70
7	53.6	53.7	1.54
15	54.9	54.9	1.58
4	57.0	57.0	0.36
12	58.4	58.3	0.30
8	61.5	61.5	0.46
16	62.8	62.8	0.42
<i>X lines</i>			
5	-13.6	..	0.0041
11	-12.5	..	0.0058
7	-3.4	-3.1 $\pi$	1.0
12	-3.4		1.0
2	-1.2	-0.9	0.9959
8	-1.1		0.9942

TABLE III (Contd.)

Transition No.*	Calculated frequency† (in cps.)	Observed frequency‡ (in cps.)	Calculated relative intensity
9	1.1	1.0	0.9942
3	1.2		0.9959
6	3.4	3.0 $\pi$	1.0
1	3.4		1.0
10	12.5	..	0.0058
4	13.6	..	0.0041
<i>Y lines</i>			
12	-14.2	..	0.0007
10	-11.9	..	0.0014
6	-1.8	-0.9	1.0
8	-1.8		1.0
5	-0.6		0.9993
4	-0.5		0.9986
3	0.5		0.9986
7	0.6		0.9993
2	1.8	1.0	1.0
1	1.8		1.0
9	11.9	..	0.0014
11	14.2	..	0.0007

\* The transition Nos. for the AB, X and Y spectra correspond to those in Tables II (a), II (b) and II (c) respectively. The expressions are to be modified in the present case by replacing C and X by X and Y respectively.

† The calculated frequencies are given with reference to  $\nu_x (= \nu_y)$  as the origin.

‡ The observed frequencies are given with respect to the centre of the XY group of lines. Average standard deviation for the observed frequency determinations is about  $\pm 0.2$  cps.

§ The peaks corresponding to these lines are not clearly identified in the spectra.

$\pi$  These lines are observed only as humps.

of lines each comprising of twelve transitions, and which are completely identical in positions and intensities with reference to their respective centres. In the observed spectrum the group of lines on the lower field consists of four lines, while the structure of the other group appears to be a little complicated probably due to the coupling of these protons with the methyl protons. However, a general resemblance between the two groups can be seen.

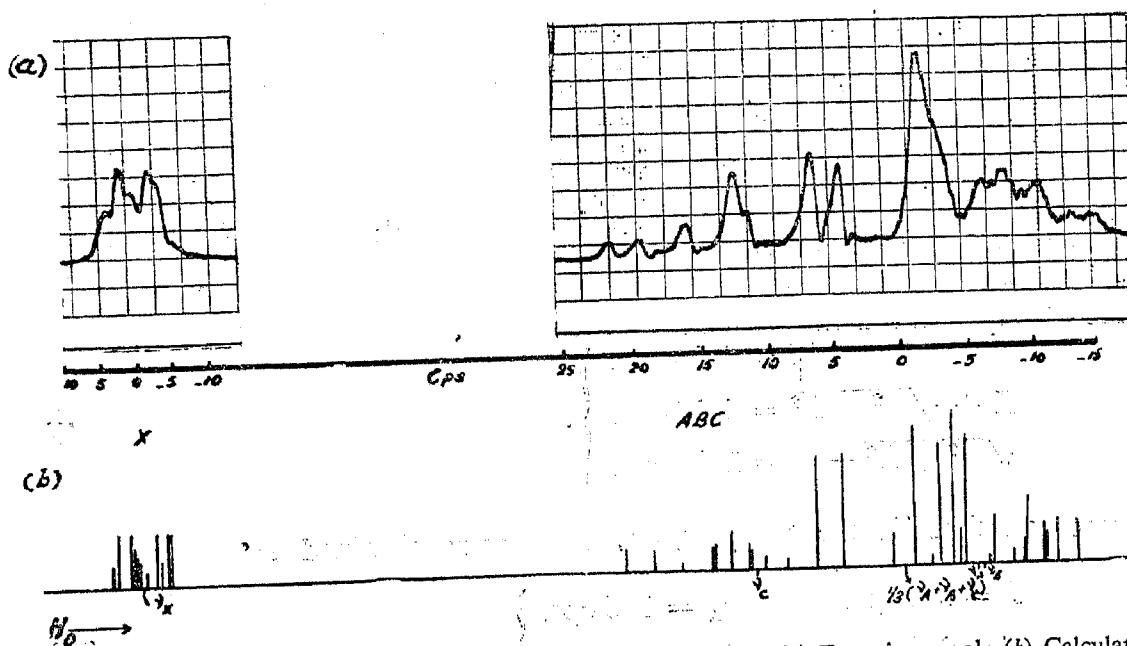


FIG. 3.  $H^1$  NMR spectrum of  $\beta$ -picoline at 40 Mc./sec. (a) Experimental; (b) Calculated. XY spectrum: 1 cm. = 6.368 cps. AB spectrum: 1 cm. = 4.221 cps.

As the coupling between the two protons *ortho* to nitrogen was observed to be very small in pyridine, 4-pyridine- $d_1^3$  and  $\beta$ -picoline (present work) it has been assumed to be equal to zero for the present analysis. The spectrum then belongs to the  $A_2X_2$  class with  $K = M$ .<sup>\*</sup> A typical half of such a spectrum consists of six transitions symmetrical with respect to the centre as given by Bernstein *et al.*<sup>9, 10</sup> The group of lines at the lower field in the observed spectrum consists of only four lines symmetrical with respect to the centre. The outer pair may be assigned to the transitions 1, 2 and 3, 4 and the inner pair to the transitions 6, 10 and 7, 11 (transition numbers as in Table 6-18 of reference 10). The other two lines (corresponding to the transitions 5, 9 and 8, 12) are comparatively weak and are

\* The transition energies and intensities were conveniently expressed in terms of  $K, L, M$  and  $N$  defined as  $K = J_A + J_X, L = J - J', M = J_A - J_X, N = J + J'$  (Fig. 6). See also references 9 and 10.

expected to occur slightly outside the pair of lines at  $\pm 3.1$  cps. from the centre. As no absorption is indicated at these positions it was assumed

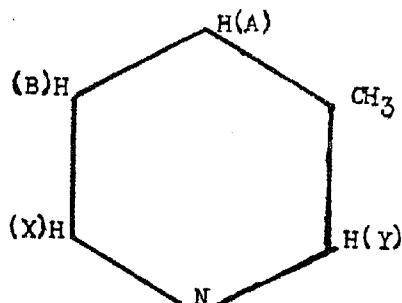


FIG. 4.  $\beta$ -picoline.

that these lines coincide with the strong lines at  $\pm 3.1$  cps. within experimental error. From the mutual separations in the observed spectrum we then get\*

$$\left. \begin{aligned} N &= 6.05 \text{ cps.} \\ K + \sqrt{K^2 + L^2} &= 6.05 \text{ cps.} \\ \sqrt{K^2 + L^2} - K &= 2.95 \text{ cps.} \end{aligned} \right\} \quad (9)$$

From equation (9) the coupling constants were obtained as

$$\left. \begin{aligned} J &= 5.1 \text{ cps.} & J_A &= 1.6 \text{ cps.} \\ J' &= 0.9 \text{ cps.} & J_X &= 0 \text{ cps.} \end{aligned} \right\} \quad (10)$$

The error involved in any of these parameters is not more than  $\pm 0.4$  cps. The calculated spectrum is shown in Fig. 5(b).

## 6. GENERAL COMMENTS

The coupling constants obtained from all these analyses do not differ in any striking manner from those in pyridine obtained by Schneider *et al.*<sup>3</sup> This is in line with the general observation that the spin coupling constants are not much sensitive to substitution. The chemical shift values also do not differ very much from the corresponding values in pyridine indicating that methyl substitution does not drastically alter the shielding of the ring protons in pyridine. The lines in all the three spectra are rather broad

\* 6.05 represents an average of the mutual separations between the intense lines in the  $A_2$  and  $X_2$  spectra. 2.95 represents the separation between the two inner components in  $X_2$  spectrum only as those in the  $A_2$  multiplet are not easily identified.

presumably due to the impurities in the samples. The accuracy of the parameters is somewhat impaired due to this reason.

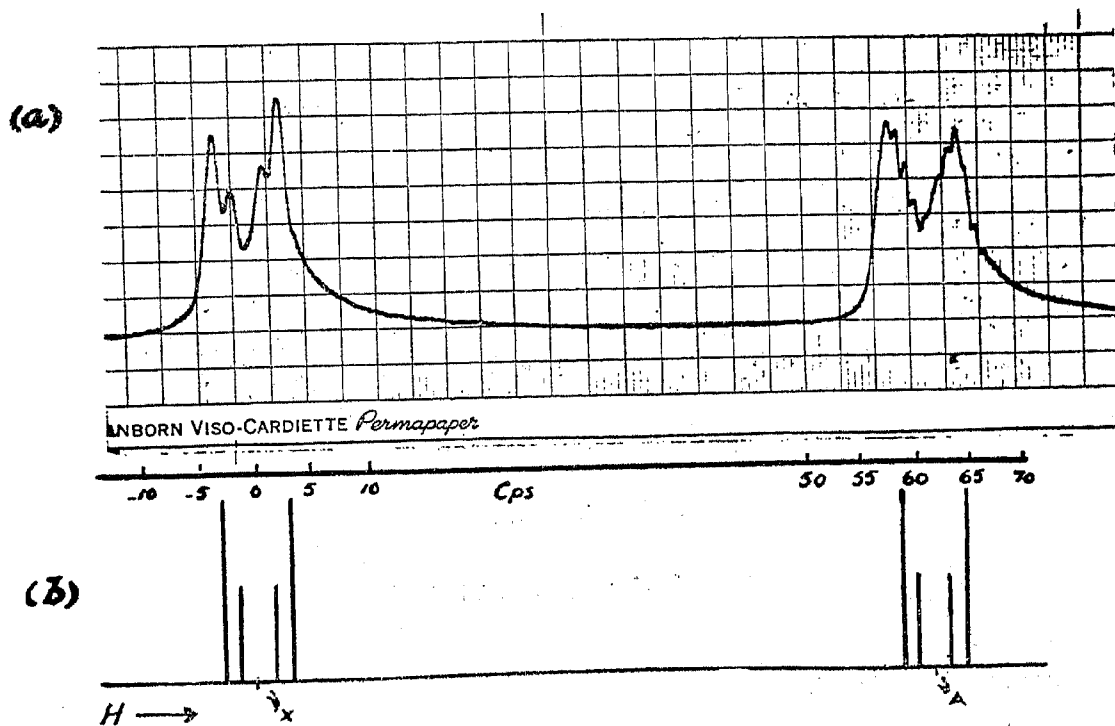


FIG. 5.  $H^1$  NMR spectrum of  $\gamma$ -picoline at 40 Mc./sec. (a) Experimental; (b) Calculated. 1 cm. = 6.491 cps.

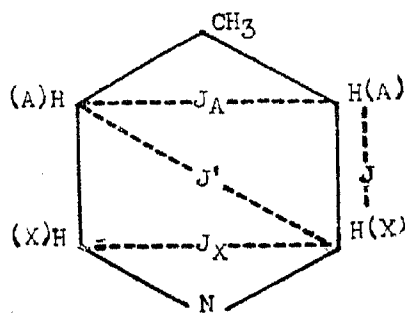


FIG. 6.  $\gamma$ -picoline.

#### ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Dr. H. Sripathi Rao, Central Fuel Research Institute, Jealgora, for providing them with the samples used in this work. Thanks are also due to the University Grants Commission for their support in developing the Microwave and Radio-frequency Laboratory at Aligarh, and to the Council of Scientific and Industrial Research for the grant of a research scheme.

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