

## MICROWAVE EVIDENCE OF RING DISTORTION IN ORTHOSUBSTITUTED PYRIDINES

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### ABSTRACT

The effect of substituents on the pyridine ring is discussed in the two molecules 2-Fluoro and 2-Cyanopyridines. A 'push in' of the carbon atom carrying the substituent is consistent with the observations of Sorensen and Nygaard in their work on Cyano and Fluorobenzenes. To account for the increase in  $I_a$  of 2-Cyanopyridine, an 'opening up' of the ring adjacent to the substituent has been postulated and explained as being due to the large contribution from the ionic resonance structures.

### INTRODUCTION

THE effect of a substituent on the benzene ring structure was first investigated by Bak<sup>1</sup> and his co-workers. From a study of a number of isotopic substituted species of cyanobenzene, they concluded that the benzene ring is distorted to some extent. Later L. Nygaard *et al.*<sup>2</sup> gave more details of the magnitude of distortion in the benzene ring from an analysis of a number of isotopic species of fluorobenzene. Recently, Casado *et al.*<sup>3</sup> by improving the accuracy of their experimental results on cyanobenzene concluded that the effect of cyano group on the benzene ring geometry is of the same nature as in fluorobenzene. Using the data of Bak *et al.*<sup>4</sup> for pyridine structure and the bond lengths for the fluoro and cyano group as given in references 2 and 3, a distortion in the pyridine ring geometry due to the substituents, has been observed by us.

### ANALYSIS OF DATA

The microwave spectra of 2-fluoropyridine<sup>5</sup> and 2-cyanopyridine<sup>6</sup> have been reported recently. The rotational constants of these molecules are given in Table I.

TABLE I

2-Fluoropyridine	2-Cyanopyridine
$A=5870.921 \text{ MHz}$	$A=5830.756 \text{ MHz}$
$B=2699.940 \text{ MHz}$	$B=1598.219 \text{ MHz}$
$C=1849.271 \text{ MHz}$	$C=1254.460 \text{ MHz}$

In giving a partial structure for 2-fluoropyridine so as to be consistent with the observed rotational constants, CF bond length of 1.30 Å and angle  $\text{NC}_2\text{F}$  of  $117.4^\circ$  were used. It had been assumed that the pyridine ring structure remained unaffected by fluorine substitution. The CF bond length is definitely low since Nygaard *et al.*<sup>2</sup> have shown that for an  $\text{sp}^2$  hybridized carbon, the CF bond length is 1.35 Å.

A similar assignment of partial structure for 2-cyanopyridine was attempted by changing  $\text{C}_2\text{C}_7$  bond length and  $\text{N}_1\text{C}_2\text{C}_7$  angle. For fitting the observed A value,  $\text{N}_1\text{C}_2\text{C}_7$  angle had to be changed from  $115^\circ 53'$  to about  $137^\circ$ , while for fitting the observed B value the  $\text{C}_2\text{C}_7$  bond length had to be decreased from 1.451 Å to 1.435 Å. The  $\text{C}_2 \equiv \text{N}_7$  bond length was not altered, as it remains essentially the same in many molecules<sup>7</sup>. A large change of about  $21^\circ$  in  $\text{N}_1\text{C}_2\text{C}_7$  angle seemed very unrealistic and it was therefore necessary to consider the distortion in the pyridine ring itself. Then the observed B value could be achieved by "pushing in" the  $\text{C}_2$  atom towards the ring centre along the  $\text{N}_2\text{C}_7\text{C}_2$  bond by about 0.0135 Å. At the same time, the atoms  $\text{N}_1$  and  $(\text{C}_3, \text{H}_3)$  have to be 'pulled out' of the ring along the  $\text{C}_2\text{N}_1$  and  $\text{C}_2\text{C}_3$  bonds respectively by about 0.009 Å to get a fit for the observed A value. In the case of 2-fluoropyridine, the 'push in' for  $\text{C}_2$  atom is considerably more and is of the order of 0.043 Å in agreement with Nygaard *et al.*<sup>2</sup> whereas the  $\text{N}_1, \text{C}_3, \text{H}_3$  positions are virtually unchanged. Table II gives the coordinates of 2 cyano and 2-fluoropyridines.

The consequences of these changes in 2 Cyano-pyridine compared to pyridine structure are, an increase in the  $\text{N}_1\text{C}_2\text{C}_3$  angle by about  $1^\circ$ , a small increase in the  $\text{N}_1\text{C}_6\text{C}_5$  and  $\text{C}_3\text{C}_4\text{C}_5$  angles and a decrease of about  $0.9^\circ$  in the  $\text{C}_2\text{N}_1\text{C}_6$  and  $\text{C}_2\text{C}_3\text{C}_4$  angles. Also  $\text{N}_1\text{C}_2$  and  $\text{C}_2\text{C}_3$  bond lengths have increased by about 0.0032 Å and 0.0023 Å respectively and  $\text{N}_1\text{C}_6$  and  $\text{C}_3\text{C}_4$  bond lengths have decreased by about 0.0041 Å and 0.0046 Å respectively. For 2-fluoropyridine the  $\text{NC}_2\text{C}_3$  angle has increased by  $3.4^\circ$ , the angles  $\text{C}_6\text{NC}_2$  and  $\text{C}_2\text{C}_3\text{C}_4$  have decreased by  $1.8^\circ$  and the bond lengths  $\text{C}_2\text{N}$  and  $\text{C}_2\text{C}_3$  have shrunk by 0.018 and 0.023 Å respectively. These results have been illustrated in Figs. 1 and 2.

TABLE II

2-Fluoropyridine			2-Cyanopyridine		
Atom	<i>b</i>	<i>a</i>	Atom	<i>b</i>	<i>a</i>
C (4)	0.0000	1.4151	C (4)	0.0000	1.4151
H (4)	0.0000	2.4924	H (4)	0.0000	2.4924
C (5)	-1.1974	0.7005	C (5)	-1.1974	0.7005
H (5)	-2.1526	1.2055	H (5)	-2.1526	1.2055
C (6)	-1.1416	-0.6929	C (6)	-1.1416	-0.6929
H (6)	-2.0557	-1.2761	H (6)	-2.0557	-1.2761
N	0.0000	-1.3949	N (1)	0.0000	-1.3949
		(-1.3956)		(-0.0077)	(-1.3997)
C (3)	1.1974	0.7005	C (3)	1.1974	0.7005
	(1.1980)	(0.7007)			(0.7096)
H (3)	2.1526	1.2055	H (3)	2.1526	1.2055
	(2.1532)	(1.2057)			(1.2146)
C (2)	1.1416	-0.6929	C (2)	1.1416	-0.6929
	(1.1048)	(-0.6694)		(1.1302)	(-0.6856)
F	2.2831	-1.4210	C (7)	2.3656	-1.4732
	(2.2463)	(-1.3975)		(2.3534)	(-1.4659)
			N (2)	3.3416	-2.0959
				(3.3296)	(-2.0887)

1. These co-ordinates are with respect to the pyridine principal axes system as given in Bak's paper page 364. Distances:  $C_3-F=1.354 \text{ \AA}$ ;  $C_2-C_7=1.451 \text{ \AA}$  and  $C_7-N_2=1.158 \text{ \AA}$ .

2. Values given in brackets are the modified co-ordinates which give the observed values of A, B and C.

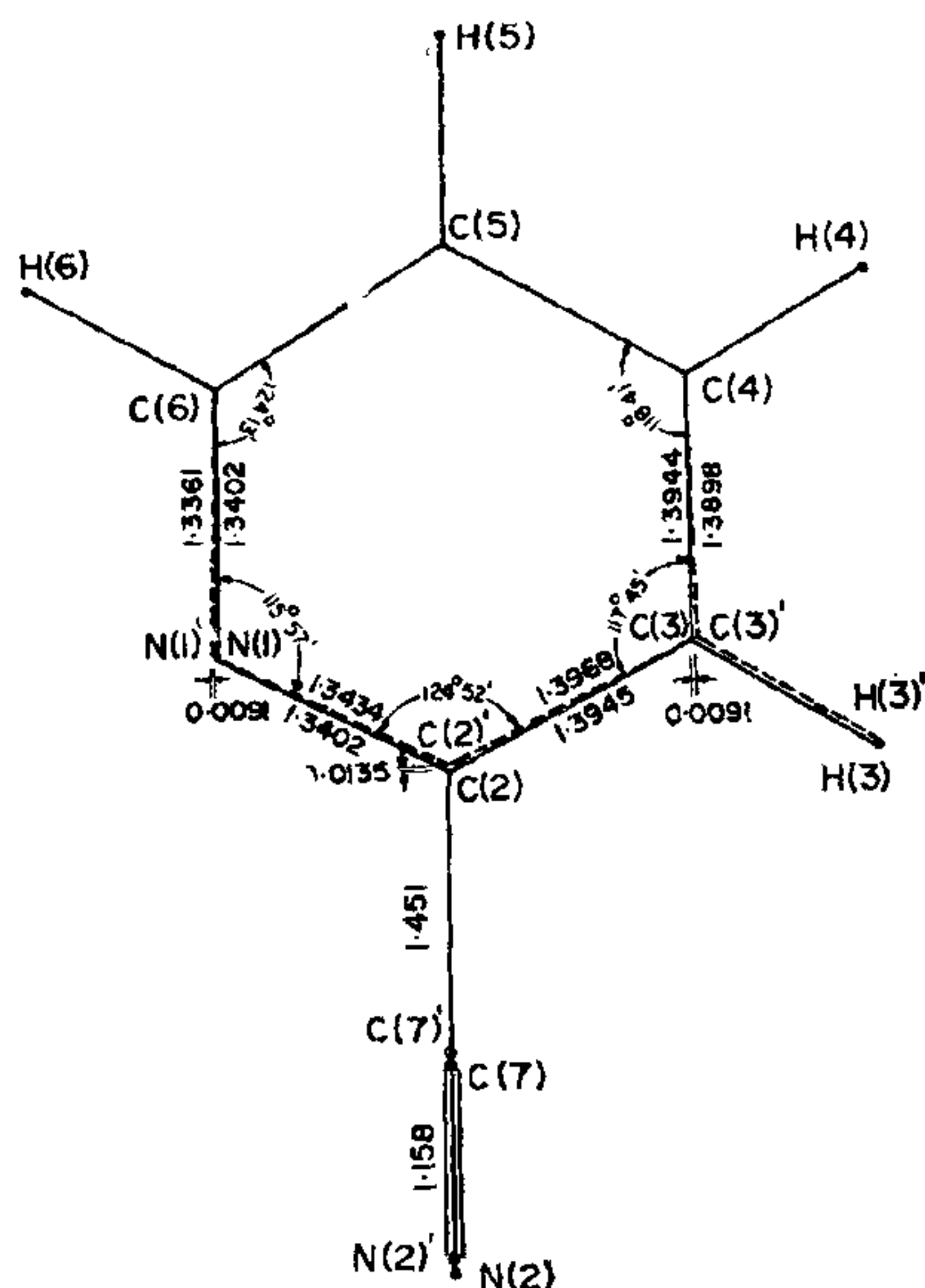


FIG. 1 2-Cyanopyridine

## DISCUSSION

The changes in the ring structure of 2-fluoropyridine are in agreement with those observed by Nygaard *et al.* on fluorobenzene. However, in the case of 2-cyanopyridine, the 'pushing in' of  $C_2$  atom is common with the observations of Sorensen *et al.* on cyanobenzene, but we observe an 'opening

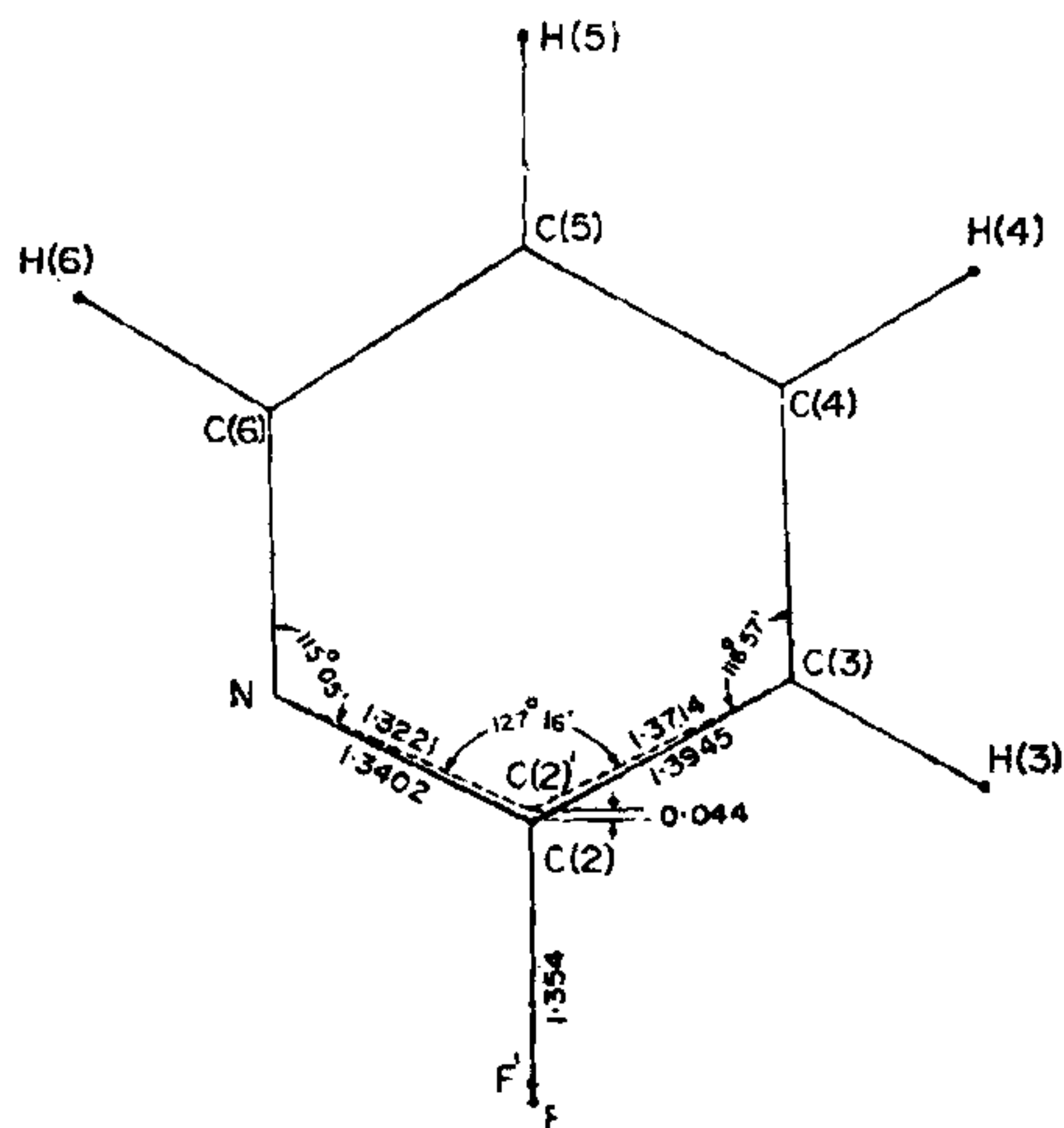


FIG. 2. 2-Fluoropyridine

up' of the ring at the  $N_1$  and  $C_3$  positions which is at variance with their observation.

The electronegativity of fluorine atom and group electronegativity of  $-C\equiv N^8$  are 4.0 and 2.8 respectively. An INDO calculation using P.A. Dobosh's<sup>9</sup> program gives electron charge densities at the site of each atom. The values for  $N_1$ ,  $C_2$  and  $C_3$  are listed in Table III for pyridine, 2-cyano and 2-fluoropyridine.



TABLE III

Atom	Pyridine	2-Cyanopyridine	2-Fluoropyridine
C <sub>2</sub>	3.899	3.874	3.595
N <sub>1</sub>	5.142	5.139	5.228
C <sub>3</sub>	4.032	4.029	4.088

A qualitative explanation for the shrinkage of bonds C<sub>2</sub>N and C<sub>2</sub>C<sub>3</sub> in the case of 2-fluoropyridine can be given on the same lines as Nygaard *et al.* by assuming a change of hybridization at the C<sub>2</sub> atom. There is an increase in the charge density in the proximity of fluorine atom because of its high electronegativity and this could be rendered possible if an enhancement of *p* character in the C<sub>2</sub> orbital pointing towards F is assumed. As a consequence of this, there must be a corresponding reduction in the *p* character in the other two  $\sigma$  bonds of C<sub>2</sub>. Or alternatively the *s* character in the two  $\sigma$  bonds has increased which means a decrease in bond length<sup>10</sup> and naturally an increase in the angle between the bonds.

But in the case of 2-cyanopyridine, it could be said that the C<sub>2</sub>N<sub>1</sub> and C<sub>2</sub>C<sub>3</sub> bonds undergo a shrinkage because of the assumption of change of hybridization at C<sub>2</sub>. In addition the contribution due to ionic resonance structures (Fig. 3) should also be taken into account.

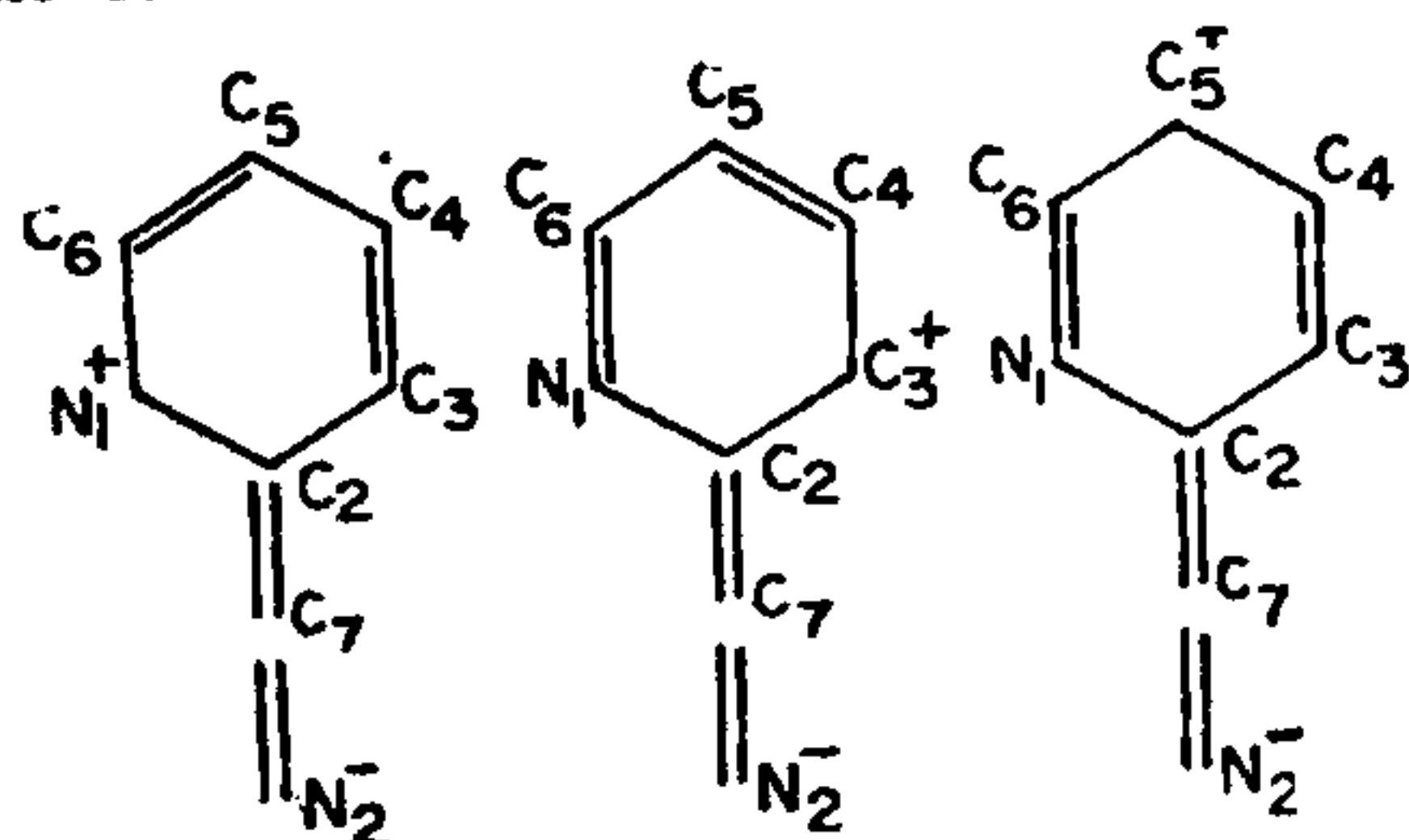


FIG. 3. 'Ionic resonance structures' of 2-cyanopyridine.

If we attach importance to these ionic resonance structures then C<sub>2</sub>N<sub>1</sub> and C<sub>2</sub>C<sub>3</sub> bond lengths should be larger and N<sub>1</sub>C<sub>6</sub> and C<sub>3</sub>C<sub>4</sub> bond lengths should be smaller than their corresponding Pyridine values. So we feel that the effects due to hybridization and the resonance structures act in such a way as to slightly increase the N<sub>1</sub>C<sub>2</sub>C<sub>3</sub> angle and the C<sub>2</sub>N<sub>1</sub> and C<sub>2</sub>C<sub>3</sub> bond lengths, but slightly decrease the N<sub>1</sub>C<sub>6</sub> and C<sub>3</sub>C<sub>4</sub> bond lengths. This is feasible only if the ring opens up at the C<sub>3</sub> and N<sub>1</sub> positions. This effect is not observed in cyanobenzene and may be due to a very small role played by resonance structures of the type shown in Fig. 3.

It may be interesting to point out here that the mesomeric moment of cyano group in 4-cyano-

pyridine is smaller than in cyanobenzene<sup>11</sup>. This has been explained as due to the polarization of the pyridine ring itself by the ring Nitrogen atom and the induction in position 4 of some additional charge under the influence of which the electron accepting capacity of cyano group decreases.

Unfortunately no data for the mesomeric moment of cyano group in 2-cyanopyridine is known. In the case of 2-cyanopyridine, perhaps the nitrogen and cyano group combine in inducing a large positive charge on their opposite side of the ring. This results in a considerable polarisation of the ring and hence an increase of the mesomeric moment compared to cyanobenzene. If this inference is correct, then there should be no 'opening up' of the ring in the case of 4-cyanopyridine.

Our discussion being highly qualitative in nature, the values for the bond lengths and angles quoted in Figs. 1 and 2 are not to be taken very seriously. But the fact remains that in order to fit the observed value of A, some sort of ring dilation has to be visualised. Of course, we have assumed that only the atoms C<sub>3</sub> and N<sub>1</sub> are affected and that too equally by the substituent. This may not be correct. We have also overlooked a possible repulsion of non-bonding orbitals of nitrogens which may cause a slight increase in N<sub>1</sub>C<sub>2</sub>C<sub>7</sub> angle. Only a detailed study of a number of isotopic species can bring out the correct picture. But to the extent our observation has served to point out a difference in the effect due to different substituents on the ring structure, the results may be useful.

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