MICROWAVE SPECTRA OF PYRIDINE AND MONODEUTERATED PYRIDINES. REVISED MOLECULAR STRUCTURE OF PYRIDINE

FERNANDO MATA, MARÍA JOSÉ QUINTANA

Physical Chemistry Department, University of Valladolid (Spain)

GEORG OLE SØRENSEN

Chemical Laboratory V, University of Copenhagen, The H.C. Ørsted Institute, DK-2100 Copenhagen (Denmark)

(Received 11 May 1977)

ABSTRACT

The microwave spectra of pyridine and its 2-D, 3-D and 4-D substituted species were reinvestigated. Nuclear quadrupole coupling and centrifugal distortion effects were considered also for the deuterated species resulting in improved values for the rotational constants of these species. Hereby more reliable information about the hydrogen positions could be obtained.

INTRODUCTION

In the microwave spectrum of pyridine several rotational transitions are appreciably split by nuclear quadrupole coupling effects. These have earlier been analyzed by Sørensen et al. [1, 2], who determined the quadrupole coupling constants of the parent as well as the four ring-substituted species, $[^{15}N]$, $[2^{-13}C]$, $[3^{-13}C]$ and $[4^{-13}C]$ pyridine. From centre frequencies of the hyperfine splitting-patterns they also determined accurate values of rotational constants, and a complete substitution structure of the pyridine ring could be obtained [2]. Since only transitions between levels with maximum J-values of four were considered centrifugal distortion effects could be neglected.

The substitution coordinates of hydrogen, however, were based on old measurements by Bak et al. [3]. At that time only broad unresolved transitions could be observed, and moreover transitions with appreciable centrifugal distortion perturbations could not be excluded. Although a correction for this was attempted the reliability of the lengths and directions of the carbon—hydrogen bonds in pyridine as given in ref. 2 are inferior compared to present day standards. For this reason we have reinvestigated the microwave spectra of the monodeuterated and parent species of pyridine aiming at a complete correction for quadrupole coupling as well as centrifugal distortion effects.

EXPERIMENTAL

The monodeuterated species of pyridine were prepared by decarboxylation of the corresponding carboxylic acids previously deuterated. This procedure was preferred as being simpler than the method of Bak et al. [3] in which monohalogenated pyridines are reduced with Zn-dust in D_2SO_4 .

For [2-D] pyridine the procedure was as follows: 34 mmoles of picolinic acid was dissolved in 6 cm³ of heavy water (D_2O). The mixture was stirred for two hours at 50°C. Excess of heavy water was removed by distillation and the solid residuum was decarboxylated by heating in a glycerol bath. The [2-D] pyridine obtained (~2 cm³, yield 47%) was distilled in vacuo and checked by IR spectrophotometry.

The [3-D] and [4-D] pyridines were prepared in a similar manner: 36 mmoles of the corresponding carboxylic acid (nicotinic and isonicotinic acid, respectively) was added to 0.625 mol of thionyl chloride. The mixture was heated for three days in a glycerol bath at 120°C. Unreacted thionyl chloride was removed by distillation (76–78°C) and the residuum was treated with petroleum ether at 45°C. The ether was removed by distillation and the liquid residuum was distilled in vacuo to isolate the corresponding acyl chloride. This compound was hydrolyzed in an excess of heavy water. The deuterated carboxylic acid so obtained (2.5 g) was mixed with 2.5 g of copper oxide and heated until decarboxylation. In both cases about 1 cm³ of deuterated pyridine was obtained (yield 22%). IR spectra showed that [3-D] pyridine was obtained together with some [2-D] and parent species. Similarly [4-D] pyridine contained pyridine.

The microwave spectra were studied using a Hewlett-Packard MRR 8460 A spectrometer. Transitions were measured at room temperature and at pressures from 1.5 to 10μ Hg. Stark fields ranging from 100 to 2000 V cm⁻¹ were applied. Frequencies were measured in the range 18–26.5 GHz calibrating against the OCS line $J = 2 \leftarrow 1$ at 24325.928 [4] and they are considered to be accurate within 0.02 MHz.

ASSIGNMENT OF SPECTRA

The assignment of observed transitions was based on precalculated spectra using the rotational constants of refs. 1 and 2. Precalculated hyperfine splitting-patterns were an additional help in assignment.

The quadrupole coupling effects were calculated from the coupling constants of the parent [2]. For the 2- and 3-deuterated species these constants were appropriately transformed to the rotated principal axis systems [5].

All *R*-lines available and *Q*-lines up to J = 29 were measured. This amounts to 55, 115, 65 and 25 transitions of pyridine, [2-D], [3-D] and [4-D]-pyridine respectively.

The list of measured frequencies and derived centre frequencies can be obtained from Fernando Mata at the address given at the beginning of this paper. Furthermore the experimental material has been deposited in the Microwave Center at the National Bureau of Standards, Washington, D.C. (U.S.A.) and with Dr. Barbara Starck, University of Ulm (W. Germany).

ROTATIONAL CONSTANTS

Rotational constants, principal moments of inertia (conversion factor 505376 MHz uÅ²), inertia defects, asymmetry parameters and centrifugal distortion constants of pyridine and its monodeuterated species are given in Table 1. They were derived from least-squares fitting to the centre frequencies using the four parameter centrifugal distortion operator [1] obtained when Dowling's relationships are applied [6]. The centrifugal distortion constants, D_1-D_4 , are the linear combinations used by Nygaard et al. [7].

As it is usually the case for planar oblate molecules D_4 is indeterminate from frequencies restricted to a narrow range. The constant was therefore fixed at -0.5 kHz throughout, this value being a fair estimate. However as emphasized earlier [7] the remaining constants are almost insensitive to the choice.

MOLECULAR STRUCTURE

The substitution coordinates of H(2) and H(3) were calculated from differences of the effective moments of inertia, I_a^0 and I_b^0 , using Kraitchman's formulae for planar molecules [8], whereas the *a*-coordinate of H(4) for symmetry reasons could be calculated from the difference in I_b^0 only. The mass scale with $m({}^{12}C) = 12$ u was used. The results are given in Table 2 including the earlier determined coordinates of the ring atoms.

The derived structural parameters are given in Table 3.

DISCUSSION

The new values of the hydrogen coordinates are not notably different from the previous [2], but, the experimental uncertainties have been essentially reduced. This means that all bond lengths and angles can now be given with equivalent precision, in Table 3, as was the main object of our investigation. Error estimates in relation to equilibrium or average structures are not affected by the revision and can be found in ref. 2.

All carbon hydrogen bonds are found 0.0007 to 0.0008 Å longer compared to the earlier results. It is therefore confirmed that C(2), H(2) is somewhat longer than the other two. Since this variation in bond length is correlated with a change in ring angle from 123.8° at C(2) to 118.5° at C(3) and C(4) an interpretation in terms of hybridization seems likely. In a carbon orbital contributing to the σ -orbital of a C—H bond the

TABLE 1

Rotational constants (MHz), asymmetry parameter, principal moments of inertia, inertial defect (uA²) and centrifugal distortion constants (kHz) of pyridine and monodeuterated pyridines with standard errors

	Pyridine	[2-D] pyrıdine	[3-D] pyridine	[4-D] pyridine
	6039.2516 ± 0.0006 5804.9116 ± 0.0006 5804.9116 ± 0.0006 0.84783313 ± 0.0000003 83.681893 ± 0.000009 87.060069 ± 0.000010 170.78061 ± 0.00004 0.03865 ± 0.00002 -4.351 ± 0.003 -0.642 ± 0.003 0.108 ± 0.003	5900.8828 ± 0.0005 5558.5214 ± 0.0005 2861.7137 ± 0.0005 0.77470068 ± 0.000000 85.644135 ± 0.000008 90.919142 ± 0.000009 176.59908 ± 0.00003 0.03580 ± 0.00003 -4.1952 ± 0.0014 0.4021 ± 0.0012 -0.5932 ± 0.0013	5889.1923 ± 0.0010 5555.0518 ± 0.0010 2858.0310 ± 0.0010 0.7795295 ± 0.000002 85.814144 ± 0.000015 90.975930 ± 0.000017 176.82663 ± 0.00003 -4.212 ± 0.003 -4.212 ± 0.003 -6.28 ± 0.003	$\begin{array}{c} 6039.9967 \pm 0.0010\\ 5420.0697 \pm 0.0009\\ 2855.8194 \pm 0.0008\\ 0.6111263 \pm 0.000002\\ 83.685423 \pm 0.000013\\ 93.241605 \pm 0.000016\\ 176.96357 \pm 0.00005\\ 0.03654 \pm 0.00005\\ -3.870 \pm 0.018\\ -0.87 \pm 0.05\\ -0.70 \pm 0.04\\ \end{array}$
Å,	-0.5 ^a	0.5ª	0.5 ^ª	0,5 ^a

^aFixed value.

TABLE 2

Substitution coordinates (A) of atoms of pyridine (with 3σ confidence limits)

Atom	a	b
N	-1.3923 ± 0.0004	
C(2)	-0.6928 ± 0.0004	1.1401 ± 0.0003
C(3)	0.6999 ± 0.0004	1.1953 ± 0.0003
C(4)	1.4124 ± 0.0002	
H(2)	-1.27588 ± 0.00001	2.05689 ± 0.00002
H(3)	1.20561 ± 0.00002	2.15254 ± 0.00004
H(4)	2.49423 ± 0.00001	

TABLE 3

Substitution structure of pyridine (with 3σ confidence limits). Distances in A and angles in degrees

$C(3), C(4), H(4) = 120.80 \pm 0.02$	N, C(2) C(2), C(3) C(3), C(4) C(2), H(2) C(3), H(3) C(4), H(4)	1.3376 ± 0.0004 1.3938 ± 0.0006 1.3916 ± 0.0004 1.0865 ± 0.0004 1.0826 ± 0.0004 1.0818 ± 0.0002	C(6), N, C(2) N, C(2), C(3) C(2), C(3), C(4) C(3), C(4), C(5) N, C(2), H(2) C(3), C(2), H(2) C(2), C(3), H(3) C(4), C(3), H(3) C(3), C(4), H(4)	$116.94 \pm 0.03 \\ 123.80 \pm 0.03 \\ 118.53 \pm 0.03 \\ 118.40 \pm 0.03 \\ 116.01 \pm 0.03 \\ 120.19 \pm 0.03 \\ 120.12 \pm 0.03 \\ 121.36 \pm 0.04 \\ 120.80 \pm 0.02 \\$
--------------------------------------	---	--	---	--

p-character increases and the s-character decreases with increasing ring angle. This follows from the condition of orthogonality between the three coplanar atomic orbitals of a carbon atom in a planar molecule [9]. However, increasing p-character results in bond lengthening as observed. Similar arguments have been presented in discussing the small C(6), N, C(2) angle [10].

REFERENCES

- 1 G. O. Sørensen, J. Mol. Spectrosc., 22 (1967) 325.
- 2 G. O. Sørensen, L. Mahler and N. Rastrup-Andersen, J. Mol. Struct., 20 (1974) 119.
- 3 B. Bak, L. Hansen and J. Rastrup-Andersen, J. Chem. Phys., 22 (1954) 2013.
- 4 N. W. Larsen and B. P. Winnewisser, Z. Naturforsch. Teil A, 29 (1974) 1213.
- 5 J. E. Wollrab, Rotational Spectra and Molecular Structure, Academic Press, New York, 1967, p. 129.
- 6 J. M. Dowling, J. Mol. Spectrosc., 6 (1961) 550.
- 7 L. Nygaard, R. L. Hansen, J. T. Nielsen, J. Rastrup-Andersen, G. O. Sørensen and P. A. Steiner, J. Mol. Struct., 12 (1972) 59.
- 8 J. Kraitchman, Am. J. Phys., 21 (1953) 17.
- 9 C. A. Coulson, Valence, Oxford University Press, London, 1961, p. 203ff.
- 10 J. Casado, L. Nygaard and G. O. Sørensen, J. Mol. Struct., 8 (1971) 211.