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PREPARATION AND MICROWAVE SPECTRA OF [^{18}O]PYRIDINE *N*-OXIDE AND DEUTERATED PYRIDINE *N*-OXIDES. COMPLETE MOLECULAR STRUCTURE OF PYRIDINE *N*-OXIDE

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ABSTRACT

[^{18}O]Pyridine *N*-oxide and the monodeuterated species have been prepared and their microwave spectra investigated for *J*-values up to 10. The complete r_s structure is determined from these data combined with data from earlier measurements on the ^{13}C- and the ^{15}N-substituted species [1]. The N—O bond length obtained here is intermediate between the typical single and double bond lengths found in other gas phase molecular structures. The structure of the C—N—C part of pyridine *N*-oxide is found to be significantly different from the corresponding part of the pyridine structure.

INTRODUCTION

The microwave spectrum of pyridine *N*-oxide was originally assigned by Brown et al. [2]. They found a small inertial defect indicating that the molecule is planar, and they determined the dipole moment, 4.13 ± 0.03 D. Snerling et al. [1] refined the values of the rotational constants by measuring *Q*-lines with *J*-values up to 40 and by correcting for centrifugal distortion effects. They also measured selected lines of the four isotopic ring substituted species from which rotational constants and a ring structure were calculated. The value of the *a*-coordinate of C(2) obtained by the substitution method was too small to be considered reliable. However, without knowledge of the *a*-coordinates of the hydrogens and the oxygen atom it was impossible to use the first moment equation to obtain a better value of the C(2) coordinate. Therefore a comparison with similar molecules was used in estimating this coordinate.

In the present work we conclude the determination of the molecular structure of pyridine *N*-oxide by the substitution method. Enriched samples of [2-D], [3-D], [4-D] and [^{18}O]pyridine *N*-oxide were prepared as described below. From measured microwave frequencies corrected for centrifugal distortion the rotational constants of Table 1 were obtained. Acquisition of rotational constants for a complete set of substituted species enabled an improved value for the small *a*-coordinate of C(2) to be obtained.

TABLE 1

Mean deviation of frequency fit, rotational constants (MHz), principal moments of inertia and inertial defect (u$\mathrm{\AA}^2$) of isotopic pyridine *N*-oxides. Standard errors of the last significant digit(s) are given in parentheses

Species	^{18}O	2-D	3-D	4-D
σ	0.032	0.036	0.044	0.030
A	5899.352(3)	5626.072(3)	5606.468(4)	5899.152(3)
B	2635.5625(10)	2782.442(3)	2751.643(4)	2667.534(3)
C	1830.2419(6)	1861.6807(8)	1845.7192(10)	1836.9027(7)
I_a	85.66637(4)	89.82751(5)	90.14161(6)	85.66927(5)
I_b	190.45190(7)	181.6304(2)	183.6634(3)	189.45441(18)
I_c	276.12526(9)	271.46224(12)	273.80979(15)	275.12399(11)
I.D.	0.00700(9)	0.0043(3)	0.0048(4)	0.0003(3)

MATERIALS AND METHODS

Preparation of samples

The deuterated species were prepared from the corresponding deuterated pyridines by oxidation with hydrogen peroxide as described in ref. 1. The monodeuterated pyridines were prepared by reduction of the corresponding bromine compounds with dideutero sulfuric acid and zinc dust according to Bak et al. [3]. The total yields for [2-D], [3-D] and [4-D] pyridine *N*-oxide were 33%, 18% and 41%, respectively, and the enrichments in all three cases were 98%.

The [^{18}O] pyridine *N*-oxide was prepared by a similar oxidation of pyridine with [^{18}O] hydrogen peroxide. The latter compound was prepared from ^{18}O-enriched water in electric discharges [4, 5]. The discharges were generated in a glass tube 2 m long and 28 mm in diameter provided with aluminum electrodes in the ends. In the preparations 2000 V AC were supplied to the electrodes and the pressure was kept at 0.5 torr giving a current of 50 mA. During a reaction period of 2 h 0.25 ml ^{18}O-enriched water was pumped through the discharge tube, and the hydrogen peroxide produced was collected in a liquid nitrogen cooled trap whereas the hydrogen formed in the reaction was removed through the pump. The mixture of hydrogen peroxide and unreacted water present in the trap after reaction was used directly in oxidizing pyridine. The yield of pyridine *N*-oxide was 134 mg corresponding to 58% (based on pyridine). By mass spectroscopy the ^{18}O-enrichment was found to be 80%.

Microwave spectra

The microwave spectra were investigated using a conventional Stark modulated (50 kHz) spectrometer equiped with a Backward Wave Oscillator source and frequency counter of type Hewlett-Packard E 40-8400 B. The frequency measurements were calibrated against the OCS line $J = 1$—2 at 24325.928 MHz [6] and are considered to be accurate to within 0.05 MHz. The frequencies were measured at room temperature at a pressure of about 0.01 torr. Stark fields ranging from 400 to 2000 V cm^{-1} were applied. The hyperfine splitting due to the ^{14}N-nuclear quadrupole coupling was only observed as a slight broadening of some of the lines which did not affect the accuracy of measurement.

For each isotopic species about 16 R-lines and 2 Q-lines with J-values up to 10 and low K_{-1} were measured. The list of frequency measurements can be obtained from the authors and has also been deposited at the Microwave Data Center at the National Bureau of Standards, Washington, D.C., U.S.A.

RESULTS

Rotational constants

The rotational constants of [^{18}O], [2-D], [3-D] and [4-D] pyridine N-oxide are given in Table 1. As indicated above they were determined from 19, 18, 16 and 18 transitions respectively, all of which were corrected for centrifugal distortion effects using the values of the centrifugal distortion constants determined for the parent species [1]. This approximate treatment introduces an uncertainty beyond the standard errors given in Table 1. However, from the analysis of the parent species we estimate that the 3σ confidence limits are appropriate. Therefore these limits are used in presenting the structural data.

TABLE 2

Substitution coordinates (Å) of the atoms in pyridine N-oxide with 3σ confidence limits of the last significant digit in parentheses, and with probable deviations from equilibrium and average coordinates

Atom	a	b	δa_e	δb_e	δa_z	δb_z
N	—0.9323(4)		—0.0027		—0.0072	
C(2)	—0.2411(7)[a]	1.1787(7)	—0.0010	0.0023	0.0029	0.0013
C(3)	1.1402(3)	1.1937(4)	0.0021	0.0021	0.0007	0.0014
C(4)	1.8626(2)		0.0014		0.0014	
O	—2.2129(1)		—0.0004		—0.0005	
H(2)	—0.8711(4)	2.0528(1)	—0.0027	0.0014	—0.0036	0.0048
H(3)	1.6437(3)	2.1513(1)	0.0014	0.0012	0.0028	0.0054
H(4)	2.9413(1)		0.0008		0.0060	

[a] Calculated from the first moment equation.

The coordinates given in Table 2 were derived from isotopic differences in I_a^0 and I_b^0 for all the nuclei except N, O, C(4) and H(4) where only I_b^0 differences were used. The small *a*-coordinate of C(2) could now be unambiguously determined by the first moment equation (the center of mass condition). The resulting value, −0.2411 Å, shows that the estimate of ref. 1, −0.249 Å, was a slight overcorrection of the substitution value, −0.229 Å. The first moment value, −0.2411 Å, can be obtained from the Kraitchman equations if we use a ΔI_b which is 0.0067 uÅ² greater than the experimental value. In a very similar situation encountered in the structural analysis of benzonitrile [7] it was stated that such a correction is a reasonable estimate of the vibrational contribution, i.e. $\Delta I_b^e - \Delta I_b^0 \sim 0.0067$ uÅ². This is a somewhat larger deviation than the usual Costain estimate (0.002 − 0.003 uÅ²) [8], but comparable with the values found in benzonitrile [7]. For this reason we have used a larger value ($\Delta I^e - \Delta I^0 = 0.005$ uÅ²) in making our general estimate of the errors, δa_e and δb_e, of the substitution coordinates in relation to the equilibrium structure (Table 2).

In Table 2 are also shown the probable deviations, δa_z and δb_z, from the average structure. These were estimated by assuming isotopic bond shortenings of 0.003 Å for C—D bonds and 0.00005 Å in other cases (for more details of this method see ref. 7).

In Table 3 are given the bond lengths and angles calculated from the sub-

TABLE 3

Distances (Å) and angles (deg.) in the substitution structure of pyridine *N*-oxide with 3σ confidence limits of the last significant digits in parentheses, and with estimated deviations from the equilibrium (δr_e) and average structure (δr_z)

	r_s	δr_e	δr_z
N—O	1.2806(4)	−0.0023	−0.0067
N—C(2)	1.3664(7)	0.0029	0.0063
C(2)—C(3)	1.3814(8)	0.0031	−0.0022
C(3)—C(4)	1.3953(4)	0.0014	0.0015
C(2)—H(2)	1.0775(8)	0.0002	0.0066
C(3)—H(3)	1.0820(4)	−0.0010	0.0044
C(4)—H(4)	1.0787(6)	−0.0006	0.0046
O—N—C(2)	120.39(3)	0	0.33
C(6)—N—C(2)	119.22(5)	−0.02	−0.67
N—C(2)—C(3)	121.01(6)	0	0.34
C(2)—C(3)—C(4)	120.56(4)	−0.06	−0.01
C(3)—C(4)—C(5)	117.64(2)	0.12	0.01
N—C(2)—H(2)	113.83(6)	−0.10	−0.51
C(3)—C(2)—H(2)	125.16(6)	0.10	0.17
C(2)—C(3)—H(3)	118.36(4)	−0.02	0
C(4)—C(3)—H(3)	121.08(4)	0.08	0.01
C(3)—C(4)—H(4)	121.18(2)	−0.06	0

stitution coordinates as well as the corrections towards the equilibrium or the average structure.

DISCUSSION

The substitution structures of pyridine *N*-oxide and pyridine [9] are compared in Fig. 1. It is evident that there are significant differences in the ring geometries, not only in the substitution structures, but, considering the error estimates in Table 3, in the equilibrium structures as well. Thus the N—C bonds are 0.03 Å longer in the *N*-oxide and the C—N—C angle is increased by 2.3° so that the nitrogen atom in the *N*-oxide seems to be regularly sp^2 hybridized. This is in perfect agreement with the inductive effects discussed for fluorobenzene [10], pyridine and benzonitrile [7], where the small C—N—C angle and the short C—N bonds in the pyridine ring were explained in terms of a preference of the lone pair electrons to occupy *s*-type atomic orbitals giving more *p*-character to the orbitals forming the C—N bonds.

Another significant structural difference is observed in the directions of the C(2)—H(2) bonds, which differ from the directions of the bisectors of the N—C(2)—C(3) angles by 2.07° in pyridine and 5.67° in pyridine *N*-oxide. Thus the oxygen atom exerts a much larger attraction on the neighbouring hydrogen atoms than the lone pair electrons.

The N—O bond is a coordinate covalent bond. At first the lengths of such bonds seem to depend highly on hybridization, Table 4. Thus we observe bond lengths of 1.217 Å in acetonitrile *N*-oxide (*sp*), of 1.2806 Å and 1.291 Å in

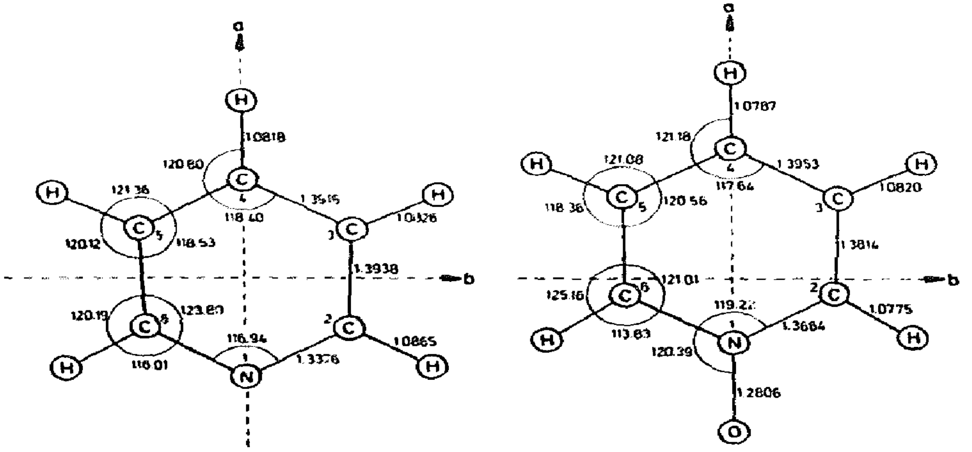

Fig. 1. Substitution structure of pyridine (left) and pyridine-*N*-oxide (right). Comparison, see text.

TABLE 4

N—O bond lengths (Å) in various compounds

Compound	Bond length	Ref.
NO	1.1506	11
CH_3CNO	1.217	12
CH_3NO	1.22	13
CH_3NO_2	1.224	14
C_5H_5NO	1.2806	This work
$O_2NC_5H_4NO$	1.291	15
$(CH_3)_3NO$	1.388	16, 17
H_2CNOH	1.408	18

pyridine *N*-oxide and in 4-nitropyridine *N*-oxide (sp^2) and about 1.39 Å in trimethylamine *N*-oxide (sp^3). A hybridization effect so large is highly unlikely and rather the differences in bond lengths must be explained in terms of electron delocalizations and bond orders. Thus the bond length of acetonitrile *N*-oxide is very similar to the double bond length in nitrosomethane, 1.22 Å, indicating that the C—N bond in acetonitrile *N*-oxide is a coordinate covalent double bond. This agrees with the similarity of this C—N bond length, 1.1671 Å [12], with the C—N double bond lengths 1.1662 Å, in acetoisonitrile [19], and 1.168 Å, in methyl isocyanate [20]. The N—O bond length in trimethylamine *N*-oxide, 1.388 Å, agrees quite well with a single bond length somewhat shortened by the effect of the formal charges, if we compare with formaldoxime, 1.408 Å. As to pyridine *N*-oxide we may therefore only conclude that the observed N—O bond length indicates considerable delocalization of the oxygen electrons towards the ring giving rise to some double bond character.

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