Infrared and Raman Spectra of Pyridine N-Oxide

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In a previous work¹⁾, we have observed the ultra-violet absorption spectrum of pyridine N-oxide vapor with a complex vibrational structure. In order to carry out the vibrational analysis of this spectrum, assignments of the fundamental frequencies of pyridine N-oxide molecule are required, but we had no datum available for this.

In the present paper, infrared and Raman spectra of pyridine N-oxide have been measured under various conditions, and assignments based on these data are presented.

Experimental

The sample of pyridine N-oxide was prepared according to the procedure of Ochiai²⁾ and was purified by repeated vacuum distillations. All precautions were taken to eliminate the absorption of atmospheric moisture by the sample.

The Raman spectrograph used in this investigation was a spectrograph with two dense flint glass prisms constructed in our laboratory, having a linear dispersion of 24 A/mm. at 4500 Å. Raman spectrum of pyridine N-oxide was obtained for both the liquid and the solution. For the liquid, hot water was circulated through the outer jacket of Wood's tube during the exposure in order to prevent the formation of crystal (the melting point of pyridine N-oxide is 59°C). For the solutions, chloroform, ethyl alcohol and water were used as solvents and concentration of each solution was about 20 g. pyridine N-oxide/20 cc. solvent. The Raman data for these conditions are listed in Table I, together with relative intensities based upon an arbitrary value of 5 for the strongest Raman line on the spectrogram. Although very broad Raman lines are also observed near 3000 cm^{-1}, they are not included in the table on account of their doubtful values.

TABLE I

INFRARED AND RAMAN FREQUENCIES OF PYRIDINE N-OXIDE (cm^{-1})

Infrared			Raman					
Solid	Chloroform solution	Ethyl alcohol solution	Liquid	Chloroform solution	Ethyl alcohol solution	Water solution	Average	Assignment
			281 (1)		286 (1)		283	$\nu_1$non-planar O bending vib.
			375 (1)	371 (0)			373	ν_2, (B_2), ring vib.
					402 (1)		402	ν_3, (A_2), ring vib.
482 w			477 (0)		480 (1)		478	ν_4, planar O bending vib.
512 w							512	
546 w				548 (0)	550 (1)		549	ν_5, (A_1), ring vib.
			635 (1)		638 (3)	641 (1)	638	ν_6, (B_1), ring vib.
679 s			687 (1)	660 (3)			674	ν_7, (B_2), non-planer H bending vib.
	803 m						803	2×402
	835 s	835 s	833 (4)	832 (4)	835 (4)	829 (3)	832	ν_8, (A_1), O stretching vib.
	880 w						880	402+478
	902 m	910 w					906	
	1015 s	1011 m	1015 (5)	1015 (5)	1015 (5)	1015 (5)	1015	ν_9, (A_1), ring vib.
	1044 w						1044	402+638
	1055 w						1055	512+549
	1096 w						1096	2×549
	1180 s	1185 s	1143 (2)	1158 (3)	1177 (3)	1177 (3)	1170	ν_{10}, (A_1), planar H bending vib.
		1240 s	1239 (3)	1250 (1)	1240 (2)		1243	ν_{11}, (B_1), planar H bending vib.
	1285 s						1285	2×638
			1312 (4)	1318 (3)	1329 (4)	1327 (4)	1321	ν_{12}, (B_1), planar H bending vib.
	1386 w						1386	549+832, 373+1015
	1402 w						1402	

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1) M. Ito and N. Hata, This Bulletin, 28, 260 (1955).

2) E. Ochiai, *J. Org. Chem.*, 18, 534 (1953).

Infrared			Raman					
Solid	Choro-from solution	Ethyl alcohol solution	Liquid	Choro-from solution	Ethyl alcohol solution	Water solution	Average	Assignment
	1473 s	1466 m	1469 (2)	1466 (2)	1466 (2)		1467	ν_{13}, (A_1), ring vib.
	1608 s	1608 m	1599 (5)	1604 (5)	1608 (5)	1606 (5)	1605	ν_{14}, (A_1), ring vib.
	1720 m	1680 m					1700	
	1864 w						1864	832+1015
	1968 w						1968	638+1321
	2050 w	2015 w					2032	2×1015
	2100 w						2100	
	2472 m	2435 w					2452	
	2926 s						2926	ν_{15}, H stretching vib.
		2990 w					2990	
	3084 m						3084	1467+1605
	3223 w						3223	2×1605

ν represents fundamental vibration.

An infrared spectrum was obtained with a Perkin-Elmer model 112 spectrometer with NaCl and KBr prisms. Measurements were made in the region of KBr for the solid sample and in the region of NaCl for the chloroform and alcohol solutions.* The frequencies of infrared absorption maxima are given in Table I, together with the Raman data. The abbreviated notations for absorption intensity, w, m and s represent weak, medium and strong, respectively.

Discussion

If the oxygen atom of pyridine N-oxide lies on a straight line connecting the nitrogen atom with the opposite carbon atom in the pyridine ring, symmetry of this molecule belongs to a point group C_{2v}, like that of the parent molecule pyridine. This structure is the most possible one and the other structures (point group C_2 and C_s) are difficult to consider. Here, assignments of the fundamental frequencies are carried out on the basis of the C_{2v} symmetry.

Ring Vibration.—As the heterocyclic ring of pyridine N-oxide is similar to that of pyridine, the ring vibration frequencies and their normal modes of the two molecules must also be similar to each other. On the other hand, the chemical similarity between benzene and pyridine is well known and electron diffraction(3), infrared and Raman data(4) show that the ring structures of benzene and pyridine are almost the same. Therefore, it is expected that the ring vibration frequencies of pyridine N-oxide should nearly coincide with those of benzene or its derivatives. That this is actually the case for the fundamental frequencies, 373(ν_2), 402(ν_3), 1015(ν_9), 1467(ν_{13}) and 1605 cm^{-1}(ν_{14}), can be recognized in Table II, where numbers in the first column denote the normal modes for the vibrations of monodeuterobenzene shown in Fig. 1(5). Accordingly, it is evident that these vibrations belong to the ring vibrations with almost the same normal

TABLE II

RING VIBRATIONS OF BENZENE, MONODEUTEROBENZENE, PYRIDINE AND PYRIDINE N-OXIDE

Normal mode a) for monodeutero-benzene (Fig. 1)	Benzene a)	Monodeutero-benzene a)	Pyridine b)	Pyridine N-oxide	Symmetry class (C_{2v})
I	405	380	374	373 (ν_2)	B_2
II	405	405	404	402 (ν_3)	A_2
III	605.6	601	604	549 (ν_5)	A_1
IV	605.6	603	604	638 (ν_6)	B_1
V	1010	1006.8	1028	1015 (ν_9)	A_1
VI	1485	1480	1485	1467 (ν_{13})	A_1
VII	1596	1591.1	1580	1605 (ν_{14})	A_1

a) Reference 5) b) Reference 4)

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3) Schomaker and Pauling, *J. Am. Chem Soc.*, 61, 1769 (1939).

4) C.H. Kline and J. Turkevich, *J. Chem. Phys.*, 12, 300 (1944).

5) C.K. Ingold and his coworkers, *J. Chem Soc.*, 1946 299 and 316.

TABLE III
HYDROGEN BENDING VIBRATIONS OF BENZENE, MONODEUTEROBENZENE, PYRIDINE AND PYRIDINE N-OXIDE

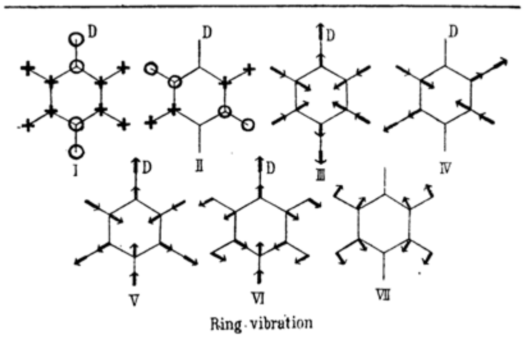
Normal mode[a] for monodeutero-benzene (Fig. 1)	Benzene[a]	Monodeutero-benzene[a]	Pyridine[b]	Pyridine N-oxide	Symmetry class (C_{2v})
VIII	671	698	652	674 (ν_7)	B_2
IX	1110	1158.2	1139	1243 (ν_{11})	B_1
X	1178	1175.6	1139	1170 (ν_{10})	A_1
XI	1326	1292	1290	1321 (ν_{12})	B_1

a) Reference 5). b) Reference 4).

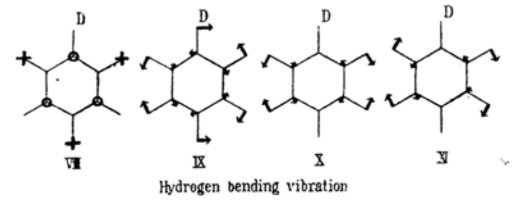
modes as those of the corresponding vibrations of monodeuterobenzene.

In addition to these, the vibrations of 549 cm^{-1}(ν_5) and 638 cm^{-1}(ν_6) are also the ring vibrations and can be interpreted as the A_1 and B_1 component vibrations deriving from the doubly degenerate E_g^+ vibration of benzene (605.6 cm^{-1}). This assignment seems to be reasonable from the fact that in monohalogenated benzenes, for example, A_1 component vibration shifts to lower frequency than 605.6 cm^{-1} and B_1 component vibration to higher frequency[6].

Hydrogen and Oxygen Bending Vibrations.—The frequency 674 cm^{-1}(ν_7) is assigned to the non-planar hydrogen bending vibration (mode VIII in Fig. 1) on the basis of its frequency value and on analogy with the frequencies of the corresponding vibrations in other molecules (Table III). In the cases of benzene and pyridine derivatives, planar hydrogen bending vibrations generally possess their characteristic frequencies in the region of 1100∼1300 cm^{-1} [6]. Pyridine N-oxide have three fundamental frequencies, 1170 cm^{-1} (ν_{10}), 1243 cm^{-1}(ν_{11}), and 1321 cm^{-1}(ν_{12}), in this region. As seen from Fig. 1, the planar hydrogen bending vibrations with X and XI normal modes might be expected to be almost unchanged in their frequencies on passing from benzene to pyridine N-oxide, but the vibration frequency with IX normal mode should be greatly changed in pyridine N-oxide as the result of a considerable contribution of planar oxygen bending vibration. Therefore, as shown in Table III, 1170 cm^{-1}(ν_{10}) and 1321 cm^{-1}(ν_{12}) are assigned to X and XI normal modes (A_1 and B_1 classes) respectively, and 1243 cm^{-1}(ν_{11}) is assigned to IX normal mode (B_1 class).



Ring vibration



Hydrogen bending vibration

Fig. 1. Normal modes of vibrations of monodeuterobenzene (after C. K. Ingold, ref. 5).

Notes: (1) Vectors perpendicular to the plane of the ring are represented by + and ○.
(2) For each point-set ○ : o = ↑ : ↑ = 2 : 1.

For 283 cm^{-1}(ν_1) and 478 cm^{-1}(ν_4), there are no comparable frequencies in the other molecules, so that these vibrations can be taken as oxygen vibration frequencies. Their frequency values suggest that 283 cm^{-1}(ν_1) is non-planar oxygen bending vibration and 478 cm^{-1}(ν_4) planar oxygen bending vibration.

Oxygen Stretching Vibration.—As 832 cm^{-1} (ν_8), which occur strongly in both infrared and Raman, has no corresponding frequency in benzene and pyridine, this vibration is also an oxygen vibration. In general, N-O stretching vibration in oxime compounds appears strongly in both infrared and Raman spectra in the region from 790 cm^{-1} to 850 cm^{-1}.[6] For example, acetoxime have this vibration at 813 cm^{-1} [7]. Therefore, 832 cm^{-1}(ν_8) can be assigned to a characteristic N-O stretching vibration, (A_1).

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[6] See, for example, Landolt-Börnstein, "Atom u Molekularphysik," 2 Teil, Molekeln 1.

[7] L. Kahovec and K. W. F. Kohlrausch, *Ber.*, 75, 627 and 1541 (1942).