

STUDIES IN HETEROCYCLIC N-OXIDES

Part I. Raman Spectra of Pyridine N-Oxide and Its Solutions

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WHILE a number of workers have studied the infra-red absorption spectra of N-oxides of tertiary amines and heterocyclic compounds, information about the Raman spectra of these compounds is relatively scarce. Thus, the only recorded instances on the Raman spectra of tertiary amine N-oxides are by Edsall,¹ Kahovec,² and Goubeau and Frömme³ who have studied the Raman spectrum of trimethylamine N-oxide and have assigned a line in the region of 950 cm.^{-1} to the N—O stretching vibration. The Raman spectra of heterocyclic N-oxides have not been recorded till recently. The present authors⁴ studied the Raman spectrum of pyridine N-oxide (II) and assigned a band at $1254 \pm 10 \text{ cm.}^{-1}$ to the N—O stretching vibration.

Raman effect studies have been extensively used in the demonstration of hydrogen bond formation with the oxygen of carbonyl compounds,⁵ but manifestations of the hydrogen bond of the type (N—O—H) do not appear to have been studied by this method. Raman spectra of pyridine N-oxide (II) in mixtures of phenol, methanol and dioxan have been recorded in the present communication with a view to studying the (N—O—H) manifestations.

EXPERIMENTAL

Pyridine N-oxide was prepared by the method of Ochiai⁶ and purified through vacuum distillation. Phenol, methanol and dioxan of high grade purity were employed. A Hilger Raman source and a Fuess glass spectrograph with a dispersion of 19 cm.^{-1} in the region of 4358 \AA were used. 4358 \AA was used as the exciting line and Hartmann diaphragm to measure the shifts of the order of a few wave numbers. As (II) is a low-melting solid, the outflowing water from the Hilger Raman source was maintained at a temperature just high enough to keep (II) in molten state.

RESULTS

The Raman frequencies of pyridine (I) and pyridine N-oxide (II) as recorded by the authors are given in Table I. The frequencies of (I) are in

good agreement with those reported earlier by Kline and Turkevich,⁷ Corrsin, Fax and Lord,⁸ and Puranik and Jaya Rao.⁹

TABLE I
Raman frequencies of pyridine and pyridine N-oxide

Pyridine cm. ⁻¹	Pyridine N→O cm. ⁻¹	Pyridine cm. ⁻¹	Pyridine N→O cm. ⁻¹
	186 (1 <i>b</i>)		1254 ± 10 (3 <i>b</i>)
	232 (1 <i>b</i>)	1284 (2 <i>b</i>)	1382 (2)
407 (1 <i>b</i>)	520 (1)	1473 (2)	1509 (1)
	553 (1)		1558 (1)
	596 (2)	1578 (5)	
602 (1 <i>b</i>)	624 (1)	1597 (2)	
653 (3)	686 (4)		1613 (8)
	730 (1)		1893 (2 <i>b</i>)
	767 (6)		2034 (2)
	841 (1 <i>b</i>)		2100 (1)
842 (1)		2455 (1 <i>b</i>)	2233 (1)
888 (2)		2494 (2 <i>b</i>)	
933 (3)			2495 (2)
974 (1)			2826 (1)
990 (8)	989 (1)	2872 (2 <i>b</i>)	2874 (2)
	1017 (3)	2913 (2)	2918 (3)
1026 (8)		2954 (2)	2954 (1)
	1050 (3)		
1067 (1 <i>b</i>)		2990 (2)	
	1104 (1)		
1143 (1 <i>b</i>)		3022 (1)	
	1157 (2 <i>b</i>)		3046 (4)
1214 (2 <i>b</i>)	1217 (3)	3053 (8)	
			3086 (1)

Changes in the relevant and important frequencies of the pyridine ring as well as the N—O stretching vibrations in mixtures of (II) with phenol, methanol and dioxan in the proportions of 1:1, 1:2 and 1:4 by volume in each solvent have been recorded and the results are listed in Table II.

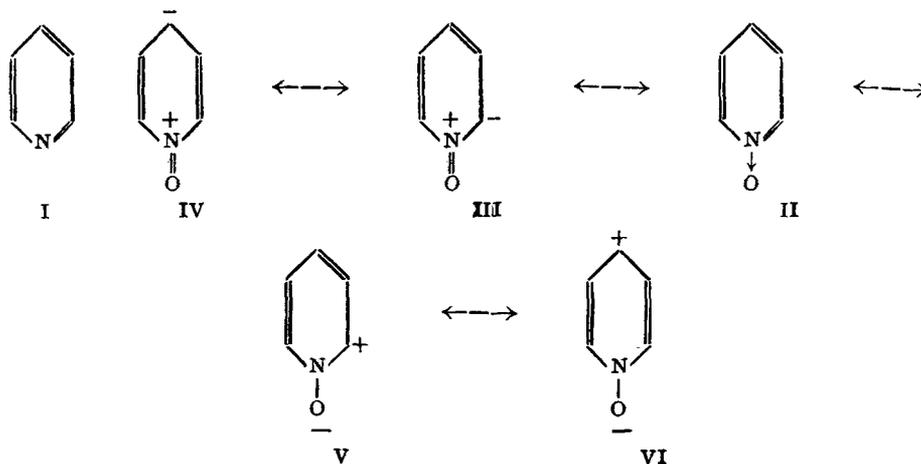
TABLE II
Raman frequencies of pyridine N-oxide in solutions

Assign- ment	Pyridine cm. ⁻¹	Pyridine N-oxide cm. ⁻¹	Pyridine N-oxide and phenol			Pyridine N-oxide and methanol			Pyridine N-oxide and dioxan		
			1:1 cm. ⁻¹	1:2 cm. ⁻¹	1:4 cm. ⁻¹	1:1 cm. ⁻¹	1:2 cm. ⁻¹	1:4 cm. ⁻¹	1:1 cm. ⁻¹	1:2 cm. ⁻¹	1:4 cm. ⁻¹
N → O	..	1254 ± 10	1270	1270	1266	1266	1269	1265	1254 ± 10	1254 ± 10	1254 ± 10
C = N	1578	1558	1558	1558	1558	1558	1558	1558	1558	1558	1558
C = C	1597	1613	1620	1618	1618	1615	1617	1617	1613	1613	1613

ASSIGNMENT OF LINES

As the double bonds are more amenable to electronic changes than others, attention has been restricted to the double bond frequencies of the pyridine ring, and to the assignment of a band to the N—O stretching vibration.

The earlier workers^{7, 8, 9} have analysed and assigned most of the lines of pyridine to different modes of ring vibrations; thus the lines at 1578 cm.⁻¹ and 1597 cm.⁻¹ have been assigned respectively to the C=N and C=C bonds of the pyridine ring.⁹



By a scrutiny of the spectra of (I) and (II) the band at $1254 \pm 10 \text{ cm.}^{-1}$ has been assigned by the authors to the N—O stretching vibration. The various canonical forms (III–VI)⁶ that are possible in (II) would give to the N—O bond considerable double bond character and hence our assignment at $1254 \pm 10 \text{ cm.}^{-1}$ to this bond. This agrees well with the infra-red absorption spectra of Blasina and co-workers¹⁰ who have assigned a band at 1242 cm.^{-1} to the N—O stretching vibration of (II) in solid and liquid states, and Wiley and Slaymaker¹¹ who have placed a band in the region of 1266 cm.^{-1} for the same bond. The difference in our assignment from those of Edsall,¹ Kahovec² and Goubeau and Fromme³ is understandable on the basis of the well-known differences in the physical and chemical properties of heterocyclic N-oxides from tertiary amine N-oxides. Our assignment also appears to be confirmed by the shift the band undergoes in mixtures of acceptor solvents.

In the region of 1550 cm.^{-1} to 1650 cm.^{-1} the authors have recorded two lines, one at 1558 cm.^{-1} and another at 1613 cm.^{-1} . The former has been assigned to C=N and the latter to C=C bonds. In (II) the presence of an oxygen atom tending to pull electrons away from the nitrogen creates a small, but definite influence towards the weakening of the C=N bond. This is indicated in the lowering of the C=N frequency from 1578 cm.^{-1} in (I) to 1558 cm.^{-1} in (II). All the possible canonical forms of (II) also tend to weaken considerably the double bond character of the C=N bond.

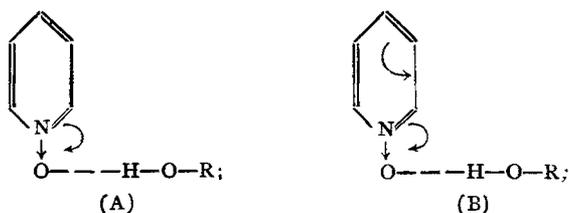
DISCUSSION OF RESULTS

A comparison of the spectra of (I) and (II) reveals clearly that most of the Raman lines of (I) are altered when it is converted into (II). In addition, in (II) there are a few new lines also, out of which one has now been assigned to N→O stretching vibration. The considerable alteration of the lines of (I) indicate a severe disturbance in the geometry of the original substance on its conversion into (II). This is obviously a consequence of the N→O bond utilising the lone pair of electrons of the tertiary nitrogen, and thus creating a positive charge on it. This causes a pull on the electrons from the attached double bond and the ring. The lowering of the C=N frequency by about 20 cm.^{-1} is a marked effect. This finds a chemical confirmation in the reactivity of the 2-methyl group in nucleophilic condensation with diethyl oxalate, a reaction which is facilitated in 2-picoline N-oxide but not in 2-picoline.¹²

An enhancement in the frequency of C=C by about 15 cm.^{-1} is another important effect of the N-oxide bond formation. This can be explained on the basis that the aromatic properties of the original pyridine ring have been

diminished; as a consequence, the ethylenic double bond characters become more prominent.

In a solution of the N-oxide (II) in neutral solvents like carbon tetrachloride no changes in the Raman lines were observed. However, on mixing (II) with acceptor solvents like phenol and methanol, changes in Raman lines are found to occur and these should be attributed to the formation of hydrogen bonds. In the earlier studies on the formation of hydrogen bonds with carbonyl compounds and the hydroxylic substances mentioned above, the C=O frequency was markedly diminished and both the original and new frequencies were found in many cases.⁵ In the case of N-oxide, however, there is an enhancement in the N→O frequency by about 15 cm.⁻¹ indicating a strengthening of the bond. This may be well explained if one visualises, that in the presence of acceptor molecules environing the N-oxide group, electrons are drawn towards the N→O group through electromeric polarisation, thus enhancing the strength of this bond as indicated in the following schemes:



The above observation finds a parallel, though caused by a mechanism exactly opposite of the present one, in the results of Katritzky and his co-workers.^{13, 14} They studied the infra-red absorption spectra of a number of 2- and 4-substituted pyridine N-oxides and showed that the electron-attracting groups in either of the positions tend to enhance the N→O frequency.



The Raman spectra of (II) with donor solvents like dioxan do not show any change. This is not unexpected as there is no possibility of hydrogen bond formation in these cases.

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SUMMARY

The Raman spectra of pyridine N-oxide and its solutions in phenol, methanol and dioxan have been recorded. The band at $1254 \pm 10 \text{ cm.}^{-1}$ has been assigned to the N—O stretching vibration. The variations in the double bond frequencies of pyridine ring, and in the frequency of N—O bond, owing to hydrogen bond formation, have been listed. On conversion of pyridine to pyridine N-oxide the various frequencies attributed to the different modes of vibrations in the pyridine ring get altered as a result of the considerable disturbance caused by the new bond.

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