VIBRATIONAL SPECTRA AND STRUCTURE OF SOME 3-HYDROXYPYRIDINE 1-OXIDE DERIVATIVES

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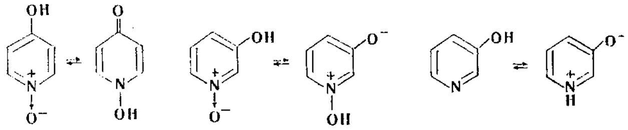
The vibrational spectra of 3-hydroxypyridine 1-oxide and its derivatives were investigated. On the basis of the assignments of the bands that characterize the OH, $\overset{+}{N} \rightarrow \overset{-}{O}$, and ring C—C bonds, it was established that these compounds exist in the crystalline state as associated zwitterions. It was shown that such associates have a more delocalized π-electron system than the monomers.

The literature contains data on the existence of commensurable amounts of the tautomeric forms in aqueous solutions of hydroxy derivatives of pyridine 1-oxide. For example, as demonstrated by PMR spectroscopy, the equilibrium a $\rightleftharpoons$ b is detected for 4-hydroxypyridine 1-oxide in water [1].



a b c d e f

The pyridone form predominates for 2-hydroxypyridine 1-oxide under the same conditions. It is apparent that a tautomeric equilibrium of the c $\rightleftharpoons$ d type is possible for 3-hydroxypyridine 1-oxide and its derivatives, in analogy with 3-hydroxypyridine (e $\rightleftharpoons$ f), which, according to the electronic spectra, develops commensurable amounts of both forms e and f in aqueous solutions [2]. In the present research we proposed to study the structure of 3-hydroxypyridine 1-oxide and its derivatives in the crystalline state by means of the vibrational spectra, which makes it possible to investigate the nature of the $\overset{+}{N} \rightarrow \overset{-}{O}$ and O—H bonds and to determine the structure of the molecule on the basis of this.

The IR spectra of compounds with an $\overset{+}{N} \rightarrow \overset{-}{O}$ coordinate bond have been quite thoroughly studied. The data on pyridine 1-oxides [3] characterize the $\overset{+}{N} \rightarrow \overset{-}{O}$ group by an intense band of stretching vibrations at 1260-1280 cm^{-1}, which can be shifted by no more than 25 cm^{-1} on formation of hydrogen bonds (see [4]).

As far as the OH group for β-hydroxypyridine derivatives is concerned, it is known [5] that it absorbs at about 3595 cm^{-1} in dilute CCl_4 solutions, but in the crystalline state it has extremely reduced frequencies of 1800, 2600, and 2900 cm^{-1} (see [6]). Sensi and Gallo [6] have proposed that this sort of shift in ν_{OH} attests to zwitterion structure f.

In the present research we investigated the spectra of 3-hydroxy derivatives of pyridine 1-oxide and their models in the crystalline state as mineral-oil pastes and KBr pellets; the spectra of solutions in CH_3OH, $CHCl_3$, or CCl_4 were obtained for some of the compounds, depending on their solubilities.

The positions of the bands and their visual intensities are presented in Table 1, and the most characteristic spectra are demonstrated in Fig. 1.

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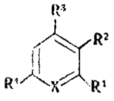
TABLE 1. Characteristic Frequencies in the Vibrational Spectra of Crystalline 3-Hydroxypyridine 1-Oxide Derivatives*



Comp.	X	R^1	R^2	R^3	R^4	ν_{OH}, cm^{-1}	ν_{N-O}, cm^{-1}	ν ring, cm^{-1}
I	N	H	OH	H	H	3010, 2920, 2500, 1875, 1810, 3650	—	1576, 1592 (vapor)
II	$\overset{+}{N}\rightarrow\overset{-}{O}$	H	OH	H	H	2200 m,b 1740 m,b	1154 vs	1570 m
III	$\overset{+}{N}\rightarrow\overset{-}{O}$	CH_3	OH	H	H	2350 m,b 1840 m,b 1780 m,b	1178 m 1212 s	1575 s
IV	$\overset{+}{N}\rightarrow\overset{-}{O}$	CH_3	OH	H	CH_3	2400 m,b 1760 m,b	1164 s 1208 s	1578 s
V	$\overset{+}{N}\rightarrow\overset{-}{O}$	CH_3	OCH_3	H	NO_2	—	1252 s	1610 m
VI	$\overset{+}{N}\rightarrow\overset{-}{O}$	H	H	NO_2	H	—	1275 s	1603 m
VII	N	CH_3	OH	NO_2	H	2600 m,b 2050 m,b	—	1585 vs
VIII	$\overset{+}{N}\rightarrow\overset{-}{O}$	NO_2	OH	H	H	2930 m,b 2400 m,b	1208 s	1580 s
IX	$\overset{+}{N}\rightarrow\overset{-}{O}$	CH_3	OH	NO_2	H	3250 m,b 3135 m,b 3115 w,b	1235 s	1622 m
X	$\overset{+}{N}-OH$ $\overset{-}{Cl}$	H	OH	H	H	2890 m,b 2550 m,b	1163 s	1638 m
XI	$\overset{+}{N}-OC_2H_5$ I^-	H	OH	H	H	3060 s,b	1152 s	1620 m
XII	$\overset{+}{N}-CH_3$ I^-	CH_3	OH	H	H	3060 s,b	—	1635 m

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*Abbreviations: ν_{OH} are the stretching vibrations of the O–H bond at 1700-3600 cm^{-1}, ν_{N-O} are the stretching vibrations of the N→O bond at 1100-1350 cm^{-1} (the most intense band), ν_{ring} is the highest frequency band of the ring skeletal vibrations, b is broad, m is medium, w is weak, and s is strong.

The IR spectra demonstrate that absorption from 3300 cm^{-1} and lower is observed for all of the investigated compounds with an OH group in the crystalline state, and it is extremely reduced (the lowest-frequency absorption bands are at 1740 and 2300 cm^{-1}) for I-IV, VII, and VIII. As already mentioned, similar spectral characteristics have been described in the pyridine series for the crystalline state of 3-hydroxypyridine [6] and were ascribed to a zwitterion structure with a hydrogen bond of the $\overset{+}{N}-H\cdots\overset{-}{O}-C$ type. Similar absorption in this region was detected in [7] for the adducts of pyridine N-oxides with acids, and it was assumed that it characterizes the formation of ion pairs with a strong intermolecular hydrogen bond of the $>\overset{+}{N}-OH\cdots\overset{-}{R}$ type (R = Cl, Br). The x-ray diffraction analysis of the adduct of pyridine N-oxide with HCl demonstrated that the absorption at 2100 cm^{-1} corresponds to an O···Cl interatomic distance of 2.84 Å [8], which indicates the formation of strong hydrogen bonds. These results make it possible to assume that the absorption at 1740, 2300, and 2500 cm^{-1} for I-IV, VII, and VIII indicates the presence of hydrogen bonds of ionic groups of the $>\overset{+}{N}-OH\cdots\overset{-}{O}-C$ type for II-IV and VIII and of the $>\overset{+}{N}-H\cdots\overset{-}{O}-C$ type for I and VII. This assumption is also confirmed by the spectral characteristics of the N–O bond.

According to the literature data [3], the stretching vibrations of the $>\overset{+}{N}\rightarrow\overset{-}{O}$ group in pyridine 1-oxides lie at 1260-1280 cm^{-1}. In fact, the most intense band in the spectra of the compounds that we studied that do not contain an OH group is observed at about 1275 cm^{-1} (VI), compared with 1252 cm^{-1} for a compound

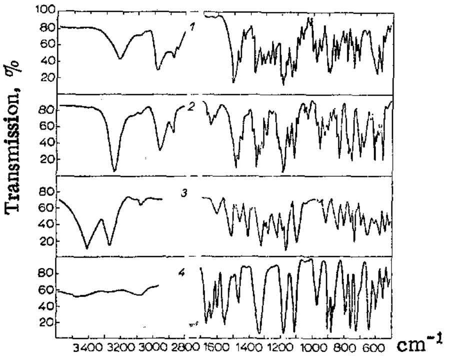

Fig. 1. IR spectra of some pyridine 1-oxides in the crystalline state (KBr pellets): 1) 3-hydroxypyridine 1-oxide (II); 2) 2-methyl-3-hydroxypyridine 1-oxide (III); 3) adduct of 3-hydroxypyridine 1-oxide with HCl (X); 4) 2-methyl-4-nitro-3-hydroxypyridine 1-oxide (IX).

with an OCH_3 group (V) and 1235 cm^{-1} for a compound with an intramolecular hydrogen bond (IX).* This band is sensitive to proton-containing solvents (1260 cm^{-1} in CCl_4 and 1210 cm^{-1} in CH_3OH). The N → O bond in the spectra of N-oxides with strong intermolecular hydrogen bonds absorbs considerably lower: 1154 cm^{-1} in the crystalline state and 1180 cm^{-1} in CH_3OH (II), 1178 and 1212 cm^{-1} (III), 1164 and 1208 cm^{-1} (IV), and 1208 cm^{-1} (VIII).

A similar spectrum is observed for salts X (1163 cm^{-1}, crystal; 1180 cm^{-1}, CH_3OH solution) and XI (1152 cm^{-1}, crystal). In addition, this absorption is absent in the spectra of pyridine derivative VII and its salt (XII). The appearance of a strong band at ~1180 cm^{-1} was also noted in [7] in the spectra of adducts of pyridine N-oxide and picoline N-oxide with HCl and HBr, and it was assigned to the N–O bond in the ion pairs.

Thus the results obtained make it possible to assert that 3-hydroxypyridine 1-oxides II-IV and VIII exist in the condensed state as ion pairs of the d type, which are associated by strong intermolecular hydrogen bonds.

An investigation of the spectra of 3-hydroxypyridine in the condensed state and in vapors established that, in addition to cleavage of the hydrogen bonds (ν_{OH} of the vapors corresponds to ~3650 cm^{-1}) and transition from the associated forms to free forms, one observes not only a change in the region of the OH bonds but also a shift in the ring stretching vibrations from 1577 to 1600 cm^{-1} (Table 1). This sort of shift in the spectra is also noted in the case of the investigated 3-hydroxypyridines. Ring vibrations at ~1580, 1530, and 1465 cm^{-1} are observed in the spectra of II-IV, VII, and VIII, the associated character of which is confirmed by ν_{OH} at 1740, 2300, 2500, and 2600 cm^{-1}, while a shift in these frequencies to 1610, 1535, and 1492 cm^{-1} (V) and 1603, 1588, and 1462 cm^{-1} (VI) is characteristic in the spectra of molecules of V and VI, which are incapable of forming hydrogen bonds. Ring vibrations of salts X-XII also appear in the high-frequency region at 1620-1640 cm^{-1}. Compounds VII and IX, which have intramolecular hydrogen bonds between the OH groups and the adjacent nitro groups, have absorption of the ring stretching vibrations at ~1600 cm^{-1} (VII in CCl_4) and 1622-1628 cm^{-1} (IX in the crystalline state or in CCl_4). It follows from the data presented that the dependence of the absorption of the pyridine ring for this series of derivatives on the associated character of the molecules is greater than its dependence on other factors.† In this case, the decrease in the frequency of the ring vibrations indicates an increase in the degree of conjugation in the system. In view of the fact that a similar pattern is observed only in self-associates and not in salts, it can be assumed that the associates have a collectivized π-electron system. In all cases, the associates constitute a more conjugated system than the monomers, which certainly promotes their stability.

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*The nature of the hydrogen bond was proved by the constancy of the absorption at 3135 cm^{-1} on successive dilution to about 10^{-3} M.

†The shift may be due to mesomeric effects and a decrease in the order of symmetry of the molecule or crystal cell.