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# THE EFFECTS OF SOLVENTS AND STRUCTURE ON THE ELECTRONIC ABSORPTION SPECTRA OF THE ISOMERIC PYRIDINE CARBOXYLIC ACID N-OXIDES

The ultraviolet absorption spectra of the carboxyl group of three isomeric pyridine carboxylic acids N-oxides (picolinic acid N-oxide, nicotinic acid N-oxide and isonicotinic acid N-oxide) were determined in fourteen solvents in the wavelength range from 200 to 400 nm. The position of the absorption maxima ($\lambda_{max}$) of the examined acids showed that the ultraviolet absorption maximum wavelengths of picolinic acid N-oxide are the shortest, and those of isonicotinic acid N-oxide acid are the longest. In order to analyze the solvent effect on the obtained absorption spectra, the ultraviolet absorption frequencies of the electronic transitions in the carboxylic group of the examined acids were correlated using a total solvatochromic equation of the form $v_{max} = v_0 + s\pi^* + a\alpha + b\beta$, where $v_{max}$ is the absorption frequency ($1/\lambda_{max}$), $\pi^*$ is a measure of the solvent polarity, $\beta$ represents the scale of solvent hydrogen bond acceptor basicities and $\alpha$ represents the scale of solvent hydrogen bond donor acidities. The correlation of the spectroscopic data was carried out by means of multiple linear regression analysis. The solvent effects on the ultraviolet absorption maximums of the examined acids were discussed.

Keywords: picolinic acid N-oxide, nicotinic acid N-oxide, isonicotinic acid N-oxide, ultraviolet absorption maximum, protic and aprotic solvents, solvatochromic effects.

Pyridine N-oxides, the group of compounds that pyridine carboxylic acids belong to, have applications in a wide range of fields including industry, medicine, biochemistry and even nano-tecnology [1-7]; therefore, there is interest in studying the structural and spectrochemical information about them.

The connection that exists between the compound structure, solvent effect and the ultraviolet absorption spectra has been a subject of many studies [8-13]. The absorption of UV light can raise the electrons in the molecule to a higher energy level. The possible electronic transition under UV light are n → π* (lone electron from the pair in a nonbonding orbital to higher level antibonding orbital), π → π* (electron from a π bond to higher level antibonding orbital) and σ → σ* (electron from a σ bond into a higher level antibonding orbital) [14,15]. The part of molecule with an ability to absorb the UV light is called the chromophore. This part of the molecule has a characteristic value of the wavelength of the absorbed UV radiation, called the absorption maximum ($\lambda_{max}$).

The π → π* transition in the carboxylic group of the three isomeric pyridine carboxylic acids (Figure 1), dissolved in a set of solvents, was analyzed in this study.
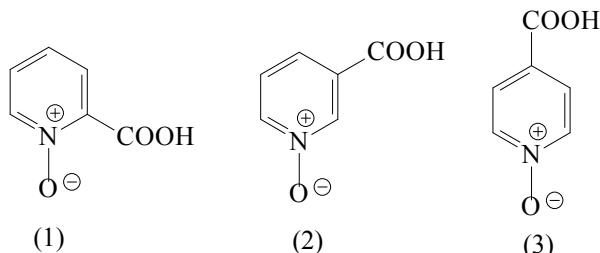


Figure 1. Picolinic acid N-oxide (**1**), Nicotinic acid N-oxide (**2**), Isonicotinic acid N-oxide (**3**).

During the excitation process, $\pi \rightarrow \pi^*$ of the one electron from the $\pi$ bond in the carbonyl (C=O) group of the carboxylic group is promoted from to an anti-bonding orbital which contains higher energy. The molecular structure or the present solvent can influence the wavelength of the absorption maximum: if $\lambda_{max}$ increases it is a batochromic shift, while if it decreases it is a hypsochromic shift. Also, batochromic shift signifies the lower energy of the electronic $\pi \rightarrow \pi^*$ transition, while the hypsochromic shift means higher energy.

The effects of solvent polarity and hydrogen bonding on the absorption spectra of the examined compounds are interpreted by means of the linear solvation energy relationships (LSER) concept, developed by Kamlet and Taft [16], using a general solvatochromic equation of the form:

$$\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta \qquad (1)$$

where $\alpha$, $\beta$ and $\pi^*$ are solvatochromic parameters; $s$, $a$ and $b$ are solvatochromic coefficients; $\nu_{max} = 1/\lambda_{max}$ is the maximum absorption frequency; and $\nu_0$ is the reference value, which is taken to be in the solvent cyclohexane, for which all the solvent parameters have the value zero [16].

In Eq. (1), $\pi^*$ is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by its own dielectric effects. The $\pi^*$ scale was selected to range from 0.00 for cyclohexanone to 1.00 for dimethyl sulfoxide. The $\alpha$ coefficient represents the solvent hydrogen bond donor (HBD) acidity, in other words it describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The $\alpha$ scale extends from 0.00 for non-HBD solvents to about 1.00 for methanol. The $\beta$ coefficient is a measure of the solvent hydrogen bond acceptor (HBA) basicity, and describes the ability of a solvent to accept a proton in a solute-to-solvent hydrogen bond. The $\beta$ scale was selected to extend from 0.00 for non-HBA solvents to about 1.00 for hexamethylphosphoricacid triamide.

## EXPERIMENTAL

Picolinic acid *N*-oxide, nicotinic acid *N*-oxide and isonicotinic acid *N*-oxide were commercial product (Fluka) of p.a. quality.

### Spectroscopic measurements

The UV spectra of the examined compounds were recorded using a Shimadzu 1700A spectrophotometer. The wavelength range was 200-400 nm. The concentrations of the examined solutions were $10^{-4}$ mol/dm$^3$. The solvents used were of high purity, designed for spectroscopic measurements.

## RESULTS AND DISCUSSION

The absorption maxima of the examined pyridine carboxylic acids N-oxides in a set of fourteen solvents are given in Table 1.

It can be noticed that the values of wavelengths of the absorption maxima increase with the number of C-atom between the carboxylic group and the N-oxy group in the ring. This batochromic shift is a consequence of the compounds structure. The negative inductive effect of the *N*-oxy group in the molecule of the picolinic acid *N*-oxide is strong on the substituent next to it, which is the carboxylic group. This effect

Table 1. The absorption maxima for the examined pyridine carboxylic acids N-oxides in various solvent

| Solvent | Picolinic acid *N*-oxide | | Nicotinic acid *N*-oxide | | Isonicotinic acid *N*-oxide | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ / nm | $\nu_{max}$ / $10^3$ cm$^{-1}$ | $\lambda_{max}$ / nm | $\nu_{max}$ / $10^3$ cm$^{-1}$ | $\lambda_{max}$ / nm | $\nu_{max}$ / $10^3$ cm$^{-1}$ |
| Methanol | 260.41 | 38.4 | 267.37 | 37.4 | 286.53 | 34.9 |
| Ethanol | 261.78 | 38.2 | 268.81 | 37.2 | 288.18 | 34.7 |
| Propan-1-ol | 263.85 | 37.9 | 271.00 | 36.9 | 289.85 | 34.5 |
| Propan-2-ol | 264.55 | 37.8 | 271.73 | 36.8 | 291.54 | 34.3 |
| 2-Methylpropan-2-ol | 266.66 | 37.5 | 273.97 | 36.5 | 290.69 | 34.4 |
| Ethylene glycol | 250.62 | 39.9 | 257.07 | 38.9 | 282.48 | 35.4 |
| Butan-1-ol | 262.46 | 38.1 | 269.54 | 37.1 | 291.54 | 34.3 |
| Pentan-1-ol | 263.15 | 38.0 | 270.27 | 37.0 | 289.85 | 34.5 |
| 2-Methylnutan-2-ol | 263.85 | 37.9 | 269.54 | 37.1 | 289.85 | 34.5 |
| Butan-2-ol | 263.85 | 37.9 | 271.74 | 36.9 | 290.69 | 34.4 |
| *N*-Methylformamide | 258.39 | 38.7 | 264.55 | 37.8 | 266.66 | 37.5 |
| Dioxane | 247.52 | 40.4 | 250.62 | 39.9 | 251.30 | 39.8 |
| Methyl acetate | 250.62 | 39.9 | 258.39 | 38.7 | 263.85 | 37.9 |
| Chloroform | 250.62 | 39.9 | 257.06 | 38.9 | 258.39 | 38.7 |

can change the electronic density and the electronic disposition in the carboxylic group and therefore cause the need for higher energy of the $\pi \rightarrow \pi^*$ transition. Furthermore, the intramolecular hydrogen bond can be formed between the carboxylic hydrogen and the oxygen from the *N*-oxy group (Figure 2) in the molecule of picolinic acid N-oxide, which additionally increases the negative inductive effect of the *N*-oxy group. This hydrogen bond has been proved and analyzed by X-ray, FTIR and NMR spectra [17]. The final electron acceptor in the system, oxygen, attracts the electrons from the σ bond strongly in order to keep the hydrogen bond.
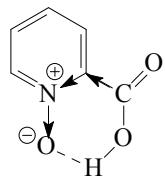


*Figure 2. The inductive effect of the N-oxy group and the hydrogen bond in the molecule of picolinic acid N-oxide.*

In the case of nicotinic acid *N*-oxide there is only the negative inductive effect of the *N*-oxy group that can influence the carbonyl group, somewhat weaker than for picolinic acid *N*-oxide and there is hardly any possibility for the formation of the intramolecular hydrogen bond. This compound therefore has longer $\lambda_{max}$ and the lower energy of the examined $\pi \rightarrow \pi^*$ transition. Even weaker negative inductive effect and no possibility for an intramolecular hydrogen bond exists in the case of the isonicotinic acid *N*-oxide. There the maximum wavelengths are the longest and the $\pi \rightarrow \pi^*$ transition energy the lowest, as it is free from the described effects.

In order to discuss the effect of solvents on the absorption spectra of the examined isomeric pyridine carboxylic acids *N*-oxide, the absorption frequencies ($\nu_{max}$) were correlated with the Kamlet-Taft solvatochromic parameters, Table 2 [18].

The obtained correlation equations were as follows:

Picolinic acid *N*-oxide:

$$\nu_{max} = 39.61 + (1.98\pm0.62)\pi^* - (2.26\pm0.48)\beta - (0.86\pm0.35)\alpha, (R = 0.957, s = 0.32, n = 14) \quad (2)$$

Nicotinic acid *N*-oxide:

$$\nu_{max} = 38.66 + (2.06\pm0.80)\pi^* - (2.28\pm0.60)\beta - (1.09\pm0.46)\alpha, (R = 0.937, s = 0.41, n = 14) \quad (3)$$

Isonicotinic acid *N*-oxide:

$$\nu_{max} = 37.64 + (3.47\pm1.46)\pi^* - (2.56\pm1.13)\beta - (3.48\pm0.84)\alpha, (R = 0.938, s = 0.75\ n = 14) \quad (4)$$

*Table 2. Solvent parameters*

| Solvent | $\pi^*$ | $\beta$ | $\alpha$ |
|---|---|---|---|
| Methanol | 0.60 | 0.62 | 0.93 |
| Ethanol | 0.54 | 0.77 | 0.83 |
| Propan-1-ol | 0.52 | 0.83 | 0.78 |
| Propan-2-ol | 0.48 | 0.95 | 0.76 |
| 2-Methylpropan-2-ol | 0.41 | 1.01 | 0.68 |
| Ethylene glycol | 0.92 | 0.52 | 0.90 |
| Butan-1-ol | 0.47 | 0.88 | 0.79 |
| Pentan-1-ol | 0.40 | 0.86 | 0.84 |
| 2-Methylbutan-2-ol | 0.40 | 0.93 | 0.28 |
| Butan-2-ol | 0.40 | 0.80 | 0.69 |
| *N*-Methylformamide | 0.90 | 0.80 | 0.62 |
| Dioxane | 0.55 | 0.37 | 0.00 |
| Methyl acetate | 0.60 | 0.42 | 0.00 |
| Chloroform | 0.58 | 0.10 | 0.20 |

From the given equation it can be seen that the here applied solvent set has a similar effect on all three examined isomeric acids. For all the examined compounds the solvent polarity/polarizability effect causes the hypsochromic shift, while the HBA and HBD solvent effects cause the batochromic shift. In other words, the energy of the $\pi^*$ electronic transition in the carboxylic group of the examined pyridine carboxylic acids *N*-oxides is raised by the solvent polarity, but lowered by its proton-donor and proton-acceptor effects. When a dipolar molecule is dissolved in a polar solvent, as it is a case in this study, the hypsochromic shift appears when the molecule is a higher dipole in the ground state, than in the excited state. With the increase of solvent polarity the more dipolar structure is better stabilized, so it can be concluded that the molecules of the examined acids are higher dipoles in the ground state and that the $\pi^*$ transition in the carbonyl group decreases their polarity. From the highest values of the coefficients for all three parameters ($\pi^*$, $\beta$ and $\alpha$) in the case of the isonicotinic acid *N*-oxide it can be seen that the solvent effect on the $\pi^*$ transition of the C=O group of this compound is the strongest, *i.e.*, that it is the most sensitive to solvent properties.

## CONCLUSION

From the analysis of the absorption spectra of the $\pi^*$ transitions of the carbonyl group in the carboxyl group of picolinic acid *N*-oxide, nicotinic acid *N*-oxide and isonicotinic acid *N*-oxide in the chosen solvent set it can be concluded that the both the structure and

the solvent effect can influence the position of the absorption maxima. The examined transition demands the highest energy in the case of picolinic acid *N*-oxide, where it is hardened by the negative inductive effect of the *N*-oxy group, and the intramolecular hydrogen bond, and the lowest energy in the case of isonicotinic acid *N*-oxide, where there is no possibility for such a hydrogen bond, and the negative inductive effect is the lowest. The analysis of solvent effects, expressed quantitatively by the Kamlet-Taft total solvatochromic equation, showed that for all three examined compounds the $\pi^*$ transition energy increases with the solvent polarity, meaning that they are lower dipoles in the excited than in the ground state.

## Acknowledgements

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NAUČNI RAD

## UTICAJ RASTVARAČA I STRUKTURE NA ELEKTRONSKE ABSORPCIONE SPEKTRE IZOMERNIH PIRIDIN-KARBOKSILNIH KISELINA *N*-OKSIDA

*UV apsorpcioni spektri pikolinske kiseline N-oksida, nikotinske kiseline N-oksida i izonikotinske kiseline N-oksida određeni su u 14 protičnih i aprotičnih rastvarača u opsegu od 200-400 nm. Položaji maksimuma apsorpcije bili su najniži za pikolinsku kiseline N-oksid, a najviši za izonikotinsku kiseline N-oksid. Da bi se analizirao uticaj ratvarača, apsorpcione frekvence su korelisane Kamlet-Taftovom jednačinom, kojom se uticaj polarnosti/polarizabilnosti, proton-donorskog i proton-akceptorskog dejstva rastvarača može kvantiativno izraziti.*

*Ključne reči: pikolinska kiselina N-oksid, nikotinska kiselina N-oksid, izonikotinska kiselina N-oksid, apsorpcioni spektri, protični i aprotični ratvarači, solvatohromni efekti.*