ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2017, Vol. 81, No. 10, pp. 1269–1272. © Allerton Press, Inc., 2017.
Original Russian Text © E.A. Illarionova, A.I. Illarionov, O.L. Nikonovich, 2017, published in Izvestiya Rossiiskoi Akademii Nauk, Seriya Fizicheskaya, 2017, Vol. 81, No. 10, pp. 1410–1413.

UV Absorption Spectra and the Physical Nature of the Optical Properties of Pyridoxine Hydrochloride

E. A. Illarionova[a], A. I. Illarionov[b], and O. L. Nikonovich[c], *

[a] *Irkutsk State Medical University, Irkutsk, 664003 Russia*
[b] *Irkutsk National Research Technical University, Irkutsk, 664074 Russia*
[c] *Irkutsk State University of Railway Engineering, Irkutsk, 664074 Russia*
**e-mail: nikonovich_ol@ irgups. ru*

Abstract—A study of the nature of electronic transitions in different structural forms of pyridoxine hydrochloride molecule shows that the maxima in experimental absorption spectra at wavelengths 244 ± 1 nm, 310 ± 1 nm (pH 12.5), 291 ± 1 nm (pH 1.1, pH 4.1), 258 ± 1 nm, 291 ± 1 nm, and 324 ± 1 nm (pH 4.15) are, along with the corresponding lines in theoretical spectra, due to electron transitions from occupied molecular *p*-orbitals localized on the nitrogen atoms in the structure of pyridine rings to the vacant *p*-orbitals of double C=N bonds.

DOI: 10.3103/S1062873817100136

INTRODUCTION

Pyridine derivatives that are heterocyclic nitrogen-containing compounds find wide application in the fields of nano- [1] and optoelectronics [2], medicine, and other branches of science and technology.

One such compound is pyridoxine hydrochloride ($C_8H_{11}NO_3 \cdot HCl$), which was first isolated in 1938 from liver, yeast, and bran, and was synthesized the same year. Its structure, 2-methyl-3 hydroxy-4,5-di-(oximato)-pyridine (Fig. 1), was chemically determined in 1939.

Pyridoxine hydrochloride is a white crystalline powder with a melting point of 214°C and a density of 1.353 g cm^{-3} [3]. This substance is readily soluble in water, barely soluble in alcohol, and virtually insoluble in ether [3]. Pyridoxine hydrochloride crystallizes into an orthorhombic lattice with point symmetry group *mm*2 (space group $Pn2_1a$) [4]. The lattice parameters are $a = 12.377$ Å, $b = 4.652$ Å, $c = 14.112$ Å, $z = 4$, and $V = 812.54$ (Å)^3 [5]. Pyridoxine hydrochloride is a form of vitamin B_6. In neutral solutions, $C_8H_{11}NO_3 \cdot HCl$ has a neutral uncharged form [6]; protonation in the structure of the pyridine ring, which is typical of all derivatives of pyridine, occurs at pHes of less than 6 (acidic solutions); in solutions with pHes from 7 to 10 (alkaline solutions), the N–H bonds are deformed [6].

The aim of this work was to explain the experimental absorption spectra we obtained in [7–9]. We therefore studied the nature of electronic transitions in a pyridoxine hydrochloride molecule in the ultraviolet region using the ZINDO/S quantum mechanical approach.

EXPERIMENTAL

The absorption spectra of pyridoxine hydrochloride in [7–9] were measured in solutions of the test substance in purified water, a 0.1 M solution of hydrochloric acid, a 0.1 M solution of sodium hydroxide, and 95% ethanol. The solutions were obtained via serial dilution. We first diluted 0.05 g of pyridoxine hydrochloride in 100 mL of distilled water. Then 1 mL of the resulting solution was placed in a 50 mL capacity measuring flask filled with a given solvent. The concentration of pyridoxine hydrochloride in the solution was thus 0.001%, allowing us to study absorption in the UV and visible regions in the working range of the spectrophotometer's optical density ($D = 0.5$–0.7).

Our earlier studies of pyridoxine hydrochloride absorption spectra showed that the absorption spectrum at pH 4.1 and 1.1 (solvents, 95% ethyl alcohol and 0.1 M hydrochloric acid, respectively) is characterized by a single absorption band with a maximum at 291 ± 1 nm (Fig. 2, curves *1, 3*) [7–9]. At pH 4.2 (solvent, distilled water), the spectrum has three absorption maxima at 258 ± 1, 291 ± 1, and 324 ± 1 nm (Fig. 2, curve *4*). At pH 12.5 (solvent, 0.1 M sodium hydrox-

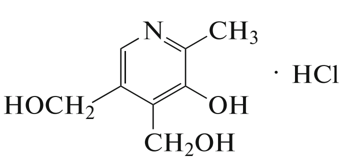


Fig. 1. Structural formula of a pyridoxine hydrochloride molecule.

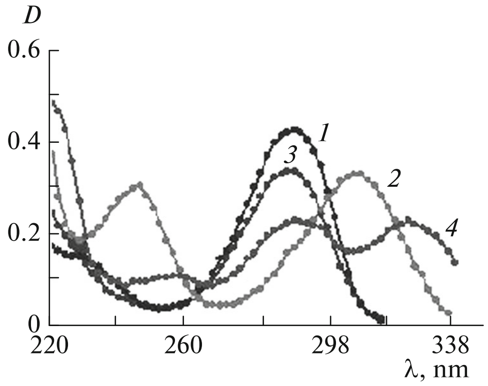


Fig. 2. Optical absorption spectra of pyridoxine hydrochloride in (*1*) a 0.1 M solution of hydrochloric acid, (*2*) a 0.1 M solution of sodium hydroxide, (*3*) 95% ethyl alcohol, and (*4*) distilled water.

ide), the spectrum is characterized by two absorption bands with maxima at 244 ± 1 and 310 ± 1 nm (Fig. 2, curve *2*).

Pyridoxine hydrochloride is a derivative of pyridine (Fig. 1) and, like ethionamide and prothionamide, has absorption bands due to transitions in the pyridine ring. However, the pyridoxine hydrochloride molecule contains a great many auxochrome substituents (Fig. 1) that are transparent in the studied spectral range and shift the absorption bands of pyridine to the long-wavelength region [10].

Pyridoxine hydrochloride in different pH solutions has different ionized forms. According to our experimental spectra, pyridoxine hydrochloride in hydrochloric acid (pH 1.1) and ethanol 95% (pH 4.1) exists in the form of peridin ions (Fig. 3b) [6]. As a rule, the optical properties of substances have practical applications in the range of near UV to near IR wavelengths. The electronic absorption spectra were therefore studied in the range of 220 to 400 nm. The maximum of the *p*-band in the solution of hydrochloric acid is at a wavelength of less than 220 nm (in the short wavelength region of the spectrum), and this absorption band is not observed in the experimental spectrum. The α-band lies at 291 ± 1 nm. According to the measured spectra, pyridoxine hydrochloride in a 0.1 M solution of sodium hydroxide (pH 12.5) exists in two forms: that of a phenolate anion (Fig. 3a) and base (Fig. 1). The maximum of the *p*-band is not seen in the measured absorption spectra of the phenolate-anion and base forms. The maximum of the α-band of pyridoxine hydrochloride lies at 310 ± 1 and 244 ± 1 nm for the phenolate-anion and base forms, respectively. Our study of the absorption spectra showed that in distilled water (pH 4.15), pyridoxine hydrochloride exists in three forms. As a result, the maximum of the α-band lies at 258 ± 1, 291 ± 1, and 324 ± 1 nm for the base, pyridine ion, and phenolate-anion forms, respectively.

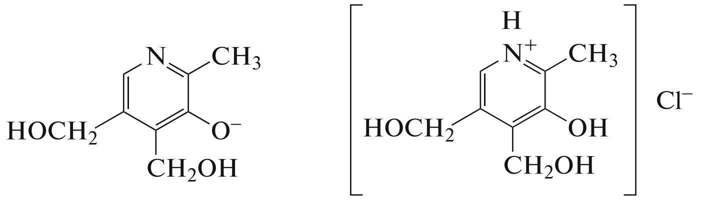
To explain the nature of the absorption bands of pyridoxine hydrochloride, we performed theoretical studies of its absorption spectra using the ZINDO/S quantum mechanical approach.

Because the pyridoxine hydrochloride in a test solution can exist in various forms, the spectral characteristics were calculated from the interaction of configurations for the phenolate-anion, pyridine-ion, and base forms. The geometry of the molecule in these forms was obtained via MM+ molecular mechanics. The results for bond lengths and valence angles are given in Tables 1 and 2.

The calculated optical characteristics of pyridoxine hydrochloride in different forms, obtained using the ZINDO/S approximation, are given in Table 3.

Calculations of the UV absorption spectra from the interaction of configurations showed that the absorption maxima in the experimental spectra of pyridoxine hydrochloride correspond to the absorption bands of the pyridine ring.

According to our ZINDO/S calculations, the absorption line of pyridoxine hydrochloride in the form of a base at 269.07 nm is due to the transition of an electron from atomic orbital 33 (energy level, –8.61 eV) to vacant atomic orbital 34 (energy level, 0.55 eV). The absorption line of pyridoxine hydrochloride in the form of a phenolate anion at 296.3 nm is due to the transition from atomic orbital 32 (energy level, –9.73 eV) to vacant atomic orbital 33 (energy level, –5.87 eV). The absorption line of pyridoxine hydrochloride in the form of a pyridine ion at 307.38 nm is due to the transition from atomic orbital 33 (energy level, –8.45 eV)



(a) (b)

Fig. 3. Structural formula of pyridoxine (a) in the form of a phenolate anion and (b) in the form of a pyridine ion.

Table 1. Theoretical bond lengths in the ground state of a pyridoxine hydrochloride molecule in different forms

Bond	Bond length for pyridoxine hydrochloride in the form of a base, Å	Bond length for pyridoxine hydrochloride in the form of a pyridine ion, Å	Bond length for pyridoxine hydrochloride in the form of a phenolate anion, Å
C(1)–C(2)	1.350	1.350	1.347
C(2)–C(3)	1.346	1.347	1.345
C(3)–N	1.263	1.266	1.264
N–C(4)	1.262	1.263	1.262
C(4)–C(5)	1.344	1.344	1.345
C(1)–C(5)	1.350	1.349	1.350
C(5)–C(7)	1.514	1.514	1.511
C(7)–O(3)	1.435	1.435	1.402
C(1)–C(6)	1.516	1.516	1.512
C(6)–O(2)	1.435	1.435	1.402
C(2)–O(1)	1.361	1.362	1.394
C(3)–C(8)	1.508	1.513	1.507
O(1)–H(1)	0.971	0.971	–
O(2)–H(2)	0.981	0.981	0.942
O(3)–H(3)	0.981	0.981	0.942

Table 2. Bond angles in the ground state of a pyridoxine hydrochloride molecule in its different forms

Bond angle	Calculated bond angle, deg	Experimental bond angle for the form of a pyridine ion, deg	Experimental bond angle for the form of a phenolate anion, deg
C(3)–N–C(4)	119.2	119.1	119.2
N–C(4)–C(5)	124.4	124.5	124.8
C(4)–C(5)–C(7)	119.9	119.9	119.8
C(4)–C(5)–C(1)	116.9	117.0	116.9
C(1)–C(5)–C(7)	123.2	123.1	123.3
C(5)–C(7)–O(3)	109.3	109.3	110.8
C(5)–C(1)–C(6)	122.2	122.3	123.1
C(5)–C(1)–C(2)	118.4	118.3	118.3
C(2)–C(1)–C(6)	119.3	119.4	119.6
C(1)–C(6)–O(2)	109.1	108.9	109.9
C(1)–C(2)–C(3)	118.5	118.9	120.4
C(1)–C(2)–O(1)	122.0	121.7	120.3
O(1)–C(2)–C(3)	119.5	119.4	119.3
C(2)–C(3)–C(8)	122.2	120.7	123.0
C(2)–C(3)–N	122.5	122.2	121.3
N–C(3)–C(8)	115.3	117.1	115.7
C(2)–O(1)–H(1)	109.6	109.7	–
C(6)–O(2)–H(2)	106.1	106.0	107.8
C(7)–O(3)–H(3)	106.2	106.2	107.8

Table 3. Calculated optical characteristics of pyridoxine hydrochloride

Form of pyridoxine hydrochloride	Calculated wavelength λ, nm	Oscillator strength f_{osc}
Phenolate anion	296.3	0.123
Pyridine ion	307.38	0.116
Base	237.39 269.07	0.121 0.134

to vacant atomic orbital 34 (energy level, –2.70 eV). According to the table of electron occupancy on atomic orbitals, orbital 33 of pyridoxine hydrochloride in the form of a base, orbital 32 in the form of a phenolate anion, and orbital 33 in the form of a pyridine ion correspond to the p_x orbital of the nitrogen atoms in the structure of pyridine rings. In addition, the table shows that orbital 34 of a molecule in the form of a base, orbital 33 in the form of a phenolate anion, and orbital 34 in the form of a pyridine ion correspond to the p_x orbital of the carbon atoms attached by double bonds to the nitrogen atoms in pyridine rings.

CONCLUSIONS

It was established that the absorption bands in the experimental spectra of pyridoxine hydrochloride at 244 ± 1 nm, 310 ± 1 nm (solvent, 0.1 M sodium hydroxide), 291 ± 1 nm (solvent, hydrochloric acid and 95% ethyl alcohol), 258 ± 1 nm, 291 ± 1 nm, and 324 ± 1 nm (solvent, distilled water) and their corresponding absorption lines in the theoretical spectra of a pyridoxine hydrochloride molecule in its different structural forms are due to the absorption of light quanta by electrons localized on the nitrogen atoms in the structure of pyridine rings. The transition proceeds from the occupied molecular p-orbitals to the vacant p-orbitals of the double C=N bonds (a π–π* transition).

REFERENCES

1. Petty, M.C., Bryce, M.R., and Bloor, G.D., *An Introduction to Molecular Electronics*, London: Oxford Univ. Press, 1995.
2. Gupta, A.A. and Saha, S.K., *Nanoscale*, 2012, vol. 4, no. 20, p. 6562.
3. *Product Specification File 42-9472-05: Pyridoxine Hydrochloride*.
4. Illarionova, E.A., *Lyuminestsentsiya i soputstvuyushchie yavleniya: trudy shkoly-seminara* (Proc. School-Seminar on Luminescence and Accompanying Phenomena), Irkutsk, 1997, p. 48.
5. Longo, J., Franklin, K.J., and Richardson, M.F., *Acta Crystallogr.*, 1982, vol. 38, p. 2721.
6. Cinta, S., Morari, C., Vogen, E., et al., *Vib. Spectrosc.*, 1999, vol. 19, p. 329.
7. Panteleeva, N.M., Illarionova, E.A., and Nikonovich, O.L., in *Trudy mezhdunarodnoi nauchnoi konferentsii "Optika kristallov i nanostruktur"* (Proc. Int. Sci. Conf. "Crystal and Nanostructure Optics"), Khabarovsk, 2008, p. 121.
8. Panteleeva, N.M., Illarionova, E.A., and Nikonovich, O.L., in *Trudy mezhdunarodnoi nauchnoi konferentsii "Optika kristallov i nanostruktur"* (Proc. Int. Sci. Conf. "Crystal and Nanostructure Optics"), Khabarovsk, 2008, p. 36.
9. Nikonovich, O.L., Illarionov, I.A., Illarionova, E.A., and Starchenko, A.A., *Izv. Vyssh. Uchebn. Zaved., Fiz.*, 2011, vol. 54, no. 2/2, p. 227.
10. Sverdlova, O.V., *Elektronnye spektry v organicheskoi khimii* (Electron Spectra in Organic Chemistry), Lelingrad: Khimiya, 1973.

Translated by V. Alekseev