

Influence of fluorination of pyridine radical on the spectral luminescent and physico-chemical properties of 4-aminopyridine

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The effect of substitution of the fluorine atoms on spectral, geometric, and photophysical characteristics, as well as proton-donating and proton-accepting properties of free aminopyridine molecules is studied by the methods of electron spectroscopy and quantum chemistry. Energy levels of singlet and triplet states of 4-aminopyridine and 4-aminotetrafluoropyridine are calculated. For 4-aminopyridine and 4-aminotetrafluoropyridine, the band in the middle spectral region is shown to be formed by several electronic transitions of different type and intensity.

Introduction

Organofluoric compounds have unique properties. They are chemically active and thermally stable. Fluorinated substances have found wide application as oils, dielectrics, heat carriers, surfactants, and medications. They have allowed obtaining solutions of some specific problems in chemistry and chemical technology, in power industry, electrotechnology, electronics, fiber optics, and medicine. The study of properties of the organofluoric compounds is also of scientific significance. The use of fluorine as a structure element of organic chemistry significantly increases the number of possible organic compounds, since this offers prospects for synthesis of new substances.¹ Fluorinated compounds are considered now as new promising absorbents for gas separation and cleaning, as ozone-safe alternate materials for freons in refrigerating devices and thermal pumps. However, to realize most completely the unique properties of organofluoric compounds, it is necessary to carry out combined studies of physical and chemical properties, to find general regularities of their variation, and to determine, on this basis, the most promising compositions for synthesis.

The aim of this work was to study the effect of fluorination of pyridine ring on the spectral-luminescent and physical-chemical properties of 4-aminopyridine.

Technique of investigation

Quantum-chemical calculations of spectral characteristics of 4-aminopyridine ($C_5H_6N_2$) and 4-aminotetrafluoropyridine ($C_5H_2N_2F_4$) were carried out using the PNDO (partial neglect of differential overlap) method.² Parameters of this method were calibrated against the absorption spectra of monosubstituted benzol molecules in hydrocarbon solvents.

The efficiency of photophysical processes was estimated based on the rate constants of radiative (k_r) and nonradiative processes (internal conversion— k_{ic} , singlet-triplet conversion— k_{ST}) [Ref. 3].

The geometry of aminopyridines was taken according to Refs. 4–6. The molecular plane lied in the XY plane, and the long molecular axis coincided with the axis X of the Cartesian coordinate system.

The absorption spectra of 4-aminopyridine and 4-aminotetrafluoropyridine in isoctane were recorded in a quartz cell ($l = 0.2$ cm) on a Shimadzu UV-1601 spectrophotometer. The concentration of aminopyridines in solutions was $\sim 4 \cdot 10^{-4}$ mol/liter.

The values of the molar absorption coefficient in the peak of the absorption bands were averaged over several solutions, and the error in determination of this coefficient did not exceed 3–5%. The error in determination of band peaks was ± 0.5 nm. The oscillator strengths of electronic transitions were determined by the technique described in Ref. 7.

Discussion

Figure 1 shows the absorption bands of 4-aminopyridine and 4-aminotetrafluoropyridine in the region from 30000 to 47000 cm^{-1} . In the long-wave spectral region, absorption of these compounds is weak and manifests itself as two peaks. Thus, for 4-aminopyridine these peaks are at 34700 and 37700 cm^{-1} , while for 4-aminotetrafluoropyridine they are at 36600 and 39900 cm^{-1} . In the middle spectral region (~ 42000 – 47000 cm^{-1}) aminopyridines have a rather intense absorption band with a peak at 43100 and 44100 cm^{-1} , respectively. Thus, fluorination of the pyridine ring of 4-aminopyridine leads to a hypsochromic shift of absorption bands.

The halfwidth of the absorption bands in the middle spectral region for these compounds is roughly 4000 cm^{-1} , which suggests the presence of several electronic transitions in the molecules under study.

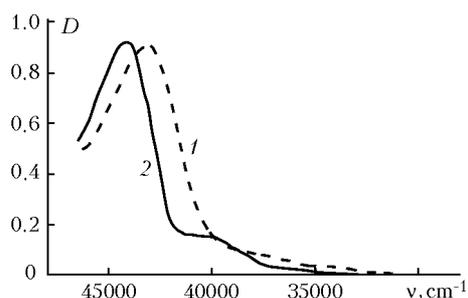


Fig. 1. Absorption spectra of aminopyridines in isoctane: 4-aminopyridine (1), 4-aminotetrafluoropyridine (2).

The quantum-chemical calculations have allowed us to interpret the observed spectral manifestations of aminopyridine absorption. It follows from the calculations that the profile of the absorption bands in the long-wave spectrum is formed by transitions $S_0 \rightarrow S_1(n\pi^*)$ and $S_0 \rightarrow S_2(\pi\pi^*)$ in 4-aminopyridine and by $S_0 \rightarrow S_1(\pi\pi^*)$ and $S_0 \rightarrow S_2(n\pi^*)$ in 4-aminotetrafluoropyridine (Table 1).

It should be noted that the nitrogen atom of the pyridine ring is responsible for the greatest

contribution to formation of the state of $n\pi^*$ -type of aminopyridines. Due to the presence of 4-aminopyridine and 4-aminotetrafluoropyridine in the plane of symmetry, the transitions $S_0 \rightarrow S_2(\pi\pi^*)$ and $S_0 \rightarrow S_1(\pi\pi^*)$ for these molecules are symmetry-forbidden.³

In the middle spectral region, the calculations indicate the existence of several electronic transitions of different nature and intensity in each of the considered compounds. However, the principal contribution to the intensity of the absorption band of the molecules in this spectral region is largely due to the transitions $S_0 \rightarrow S_4(\pi\pi^*)$ in 4-aminopyridine and $S_0 \rightarrow S_3(\pi\pi^*)$ in 4-aminotetrafluoropyridine (Table 1).

Figure 2 depicts schematically the excited energy states and the rate constants of intramolecular physical processes in 4-aminopyridine and 4-aminotetrafluoropyridine. It follows from Fig. 2 that fluorination of the pyridine ring leads to significant changes in the rate constants of radiative and nonradiative processes. It can be noted that the singlet-triplet conversion for the aminopyridines under study is the main channel for the destruction of the lower singlet states.

Table 1. Spectral characteristics of absorption bands of aminopyridines in isoctane

Compound	State	Experiment		Calculation		
		E_i, cm^{-1}	f	E_i, cm^{-1}	f	P
4-aminopyridine	$S_1(n\pi^*)$	34700	0.007	36390	0.009	Z
	$S_2(\pi\pi^*)$	37700	0.014	39400	0.011	Y
	$S_3(n\pi^*)$			39790	0.000	–
	$S_4(\pi\pi^*)$	43100	0.205	43950	0.162	X
4-aminotetrafluoropyridine	$S_1(\pi\pi^*)$	36600	0.003	37490	0.001	Y
	$S_2(n\pi^*)$	39900	0.010	39930	0.008	Z
	$S_3(\pi\pi^*)$			40860	0.183	X
	$S_4(\pi\sigma^*)$	44070	0.211	42024	0.008	Z
	$S_5(n\pi^*)$			42700	0.000	–

Note. E_i is the energy, f is the oscillator strength, P is the polarization of the electronic transition.

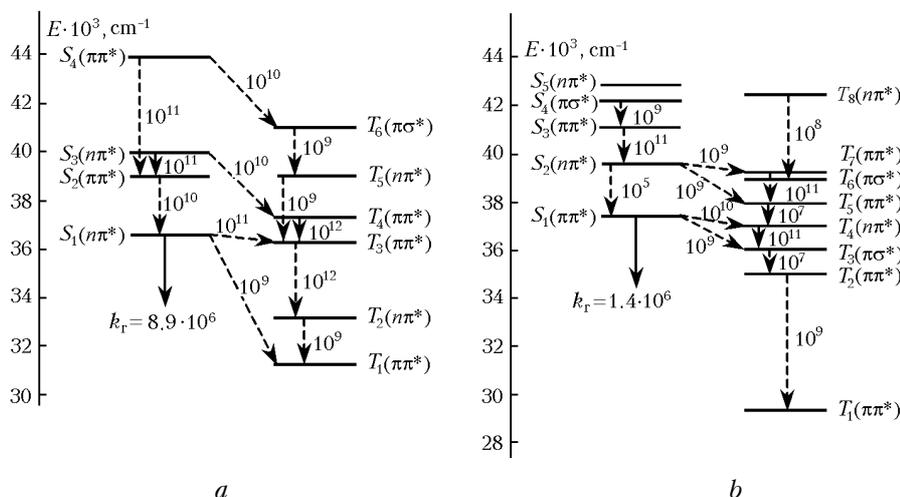


Fig. 2. Energy scheme of excited electronic states and rate constants of nonradiative processes (in s^{-1}) in 4-aminopyridine (a) and 4-aminotetrafluoropyridine (b).

Table 2. Calculated physicochemical characteristics of aminopyridines in different electronic states

Compound	State	μ , D		Q , e			P_{NH} , e
		exp.	calc.	N_{pyr}	$N_{\text{a.g.}}$	$H_{\text{a.g.}}$	
4-aminopyridine	S_0	3.93	4.83	-0.435	-0.358	0.150	0.675
	$S_1(n\pi^*)$		1.54	0.011	-0.387	0.148	0.673
	$S_2(\pi\pi^*)$		5.35	-0.480	-0.252	0.150	0.675
	$S_3(n\pi^*)$		1.73	0.225	-0.352	0.150	0.675
	$S_4(\pi\pi^*)$		7.14	-0.457	-0.152	0.151	0.675
4-aminotetrafluoropyridine	S_0	–	5.88	-0.353	-0.328	0.176	0.677
	$S_1(\pi\pi^*)$		7.94	-0.342	-0.106	0.177	0.678
	$S_2(n\pi^*)$		2.00	0.179	-0.367	0.175	0.675
	$S_3(\pi\pi^*)$		8.62	-0.404	-0.045	0.178	0.677
	$S_4(\pi\sigma^*)$		7.03	-0.208	0.008	0.178	0.676
	$S_5(n\pi^*)$		1.53	0.371	-0.321	0.176	0.676

Note: μ is the dipole moment (in D); Q is the effective atomic charge, in e; P_{NH} is the population of the NH-bond (electron density), in e; N_{pyr} is the nitrogen atom of the pyridine ring; $N_{\text{a.g.}}$ and $H_{\text{a.g.}}$ are the nitrogen and hydrogen atoms of the NH-bond of amino group.

The dipole moments of 4-aminopyridine and 4-aminotetrafluoropyridine in different excited electronic states are given in Table 2. It follows from Table 2 that our quantum-chemical calculation gives the values of dipole moment for the considered molecules that are quite close to the experimental data.⁸ As can be seen from Table 2, the dipole moment of the electronic transitions of $\pi\pi^*$ -types increases only slightly as compared with the ground state, while in the states of $n\pi^*$ -type it decreases by 2 to 3 times.

Note that fluorination of 4-aminopyridine leads to a decrease of the charge on the nitrogen atom of the pyridine ring and to the increase in the charge of the hydrogen atoms of amino group, which results in a significant change of proton-donating and proton-accepting properties of the molecule (Table 2). Table 2 gives the populations of the bonds P_{NH} of amino group, which allow us to estimate how strong this chemical bond is in the molecule at excitation.³ The increase of the bond population indicates that the chemical bond becomes shorter, while its decrease indicates that the bond becomes longer. It follows from Table 2 that fluorination leads to strengthening of the NH bond in amino group.

Thus, the experimental and quantum-chemical studies have shown that the absorption bands of 4-aminopyridine and 4-aminotetrafluoropyridine in the region of 30000–47000 cm^{-1} are formed by several electronic transitions of different nature and intensity. The states S_1 and S_3 in 4-aminopyridine, as well as S_2 and S_5 in 4-aminotetrafluoropyridine correspond to $n\pi^*$ -type, in which n -orbital is located on atomic orbitals of the nitrogen atom of the pyridine ring. The basic transitions contributing to the intensity of the absorption bands in the long-

wave and middle spectral regions are the transitions of $\pi\pi^*$ -type, and fluorination leads to the hypsochromic shift of these bands. The high electronegativity of fluorine leads to significant changes in the proton-donating and proton-accepting properties of 4-aminotetrafluoropyridine as compared to 4-aminopyridine.

Acknowledgments

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