ELECTRONIC STRUCTURE AND PROPERTIES OF PYRIDYL- AND QUINOLYLAMINES

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The π-electron structures and spectra corresponding to singlet–singlet $\pi-\pi^*$ transitions of neutral and protonated pyridyl- and quinolylamine molecules were calculated by the MO LCAO method within the semiempirical Pariser–Parr–Pople approximation with allowance for configuration interaction. It is shown that the π-electron density distribution explains the different directions of nucleophilic and electrophilic substitution reactions in the neutral and protonated heterocycle molecules. It is concluded that the character of protonation of amino-substituted quinolines is distinct.

The peculiarities of the chemical properties of 2- and 4-aminopyridines and of 2- and 4-aminoquinolines formerly compelled one to assume the existence of amine-imine tautomerism in these compounds. However, attempts to prove the existence of tautomers by various physical methods have demonstrated that all of these compounds are the ordinary amino derivatives and that their imine tautomers do not exist [1].

We have undertaken a theoretical investigation of the electronic structures of these compounds and their protonated cations. The calculations were performed by the MO LCAO method within the semiempirical approximation of the self-consistent-field method using MN, PPP-2, and Cl-1 programs [2]. The calculations were made with an M-220 computer. The empirical parameters for the calculations were taken from [3-5]. The interaction of 25 singly excited configurations was taken into account in the calculation of the energies of the excited states. The molecular diagrams of the aminopyridine molecules and their protonated cations are presented in Fig. 1. Similar diagrams for aminoquinolines are presented in Fig. 2. The calculated and experimental positions of the maxima in the electronic spectra of the compounds, which are caused by singlet–singlet transitions, are presented in Tables 1 and 2. The squares of the dipole moments (M^2), which are directly proportional to the integrals of the band intensities, and the ratios of the moments of the transitions in two mutually perpendicular directions ($\tan\alpha$), which characterize the polarization of the bands, are also presented.

A comparison of the calculated and experimental positions of the maxima of the bands of the neutral molecules demonstrates their satisfactory agreement. This again confirms the absence of tautomerism and the existence of neutral molecules in the amine form. The electronic spectra of the aminopyridine that we calculated are in satisfactory agreement with the results in [6]. In the case of aminoquinolines, except for 2- and 4-derivatives, the calculated positions of the longest-wave maxima differ from the experimental values by 20-25 nm.

Certain difficulties are encountered in the explanation of the position of the bands in the electronic spectra of the cations of the protonated aminopyridine and aminoquinoline molecules. As we demonstrated in [5], protonation of the nitrogen heterocycles is complex in nature. In some cases in acidic media, a proton adds to the nitrogen atom, which is in conformity with the usual concepts. In this case, the proton that has added to the nitrogen atom of the heterocycle is strongly bonded to this atom and interacts only weakly with the medium (type II). In other cases, the nitrogen atom of the heterocycle forms only strong hydrogen bonds in acidic media (type I). This type of protonation can also be characterized by the fact that the proton that has added to the nitrogen atom of the heterocycle retains a strong interaction with the media molecules. For example, protonation of the heterocycle can be considered to be not only addition of a proton

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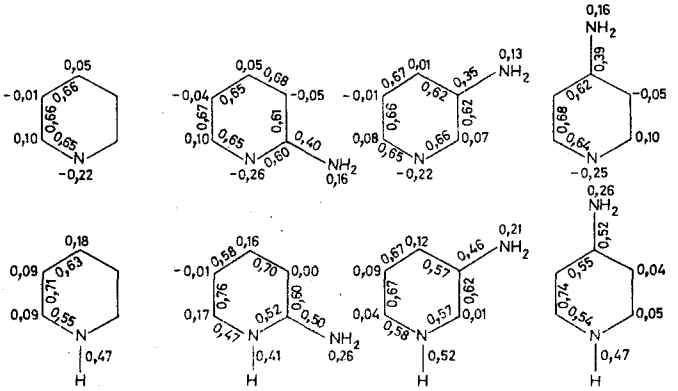

Fig. 1. π-Electron density distribution in neutral and protonated pyridine and aminopyridine molecules.

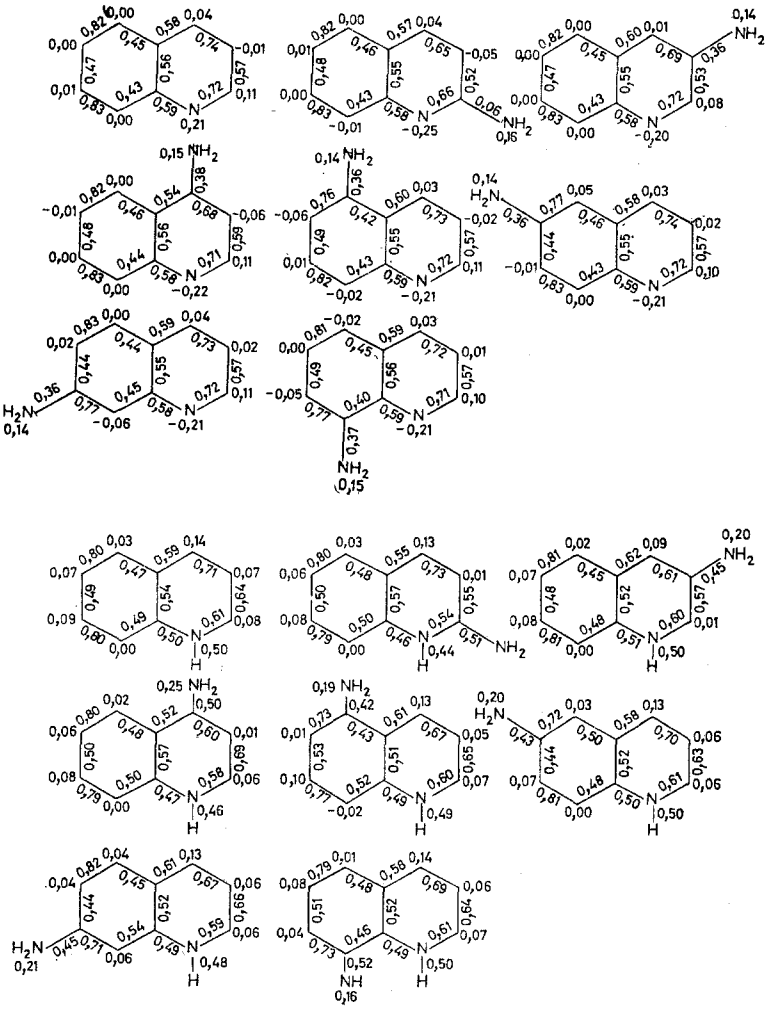

Fig. 2. π-Electron density distribution in neutral and protonated quinoline and aminoquinoline molecules.

TABLE 1. Electronic Spectra of Neutral and Protonated Pyridine and Aminopyridine Molecules

Compound	Base				Protonated base			
	λ_{th}, nm	λ_{exp}, nm	M^2, Å^2	tg α	λ_{th}, nm	λ_{exp}, nm	M^2, Å^2	tg α
Pyridine	252	251	0,14	0,004	262	260	0,42	0,004
	198	—	0,02	44,5	204	—	0,003	16,00
2-Aminopyridine	276	287[10]	0,33	0,16	299	300[9]	1,03	0,11
	224	231	0,80	1,02	231	—	0,18	1,90
	187	188	0,75	0,83	201	—	1,45	2,53
3-Aminopyridine	280	292[10]	0,28	0,44	335	317[12]	0,53	0,58
	231	232	0,71	0,67	258	250	0,16	0,61
	194	194	0,89	6,89	220	—	1,80	0,81
4-Aminopyridine	262	260[10]	0,004	0,02	277	263[9]	1,27	2076
	233	233	0,80	342	263	—	0,04	0,01
	197	199	1,20	0,01	223	—	0,92	0,001

TABLE 2. Electronic Spectra of Neutral and Protonated Quinoline and Aminoquinoline Molecules

Compound	Base				Protonated base			
	λ_{th}, nm	λ_{exp}, mm	M^2, Å^2	tg α	λ_{th}, nm	λ_{exp}, nm	M^2, Å^2	tg α
Quinoline	301	313	1,01	0,01	315	313	0,42	0,08
	255	270	0,09	1,44	282	—	0,02	5,50
	223	225	2,00	0,12	237	233	1,63	0,04
	215	—	1,53	2,94	221	—	0,65	16,49
2-Aminoquinoline	318	310	0,35	0,22	348	310—340	0,91	0,44
	267	—	0,47	0,33	329	—	0,31	0,12
	232	—	2,14	0,49	269	260	1,98	0,15
	227	—	1,01	5,74	250	—	0,60	2,55
	217	—	1,42	0,32	—	—		
3-Aminoquinoline	323	338	0,25	0,54	396	375	0,61	1,01
	271	—	0,38	0,18	332	312	0,10	33,06
	238	—	1,55	1,19	286	260	0,62	0,18
	233	—	2,11	0,03	242	—	0,33	1,47
4-Aminoquinoline	309	295	0,01	0,10	340	315	0,48	7,05
	275	—	0,55	1,78	314	300	0,10	1,08
	232	—	0,90	1,56	281	—	1,02	0,70
	225	220	1,43	0,72	254	240	1,58	0,10
					240	—	0,58	
7-Aminoquinoline	320	350	0,19	0,52	409	395	0,89	0,19
	272	285	0,28	0,10	330	—	0,10	0,99
	239	245	1,67	0,58	287	290	1,91	0,57
	226	—	2,20	0,19	257	250	0,42	0,18
					239	—	0,42	1,42
5-Aminoquinoline	315	335	0,02	0,41				
	289	—	0,46	8,00				
	246	250	1,82	0,07				
	224	—	0,71	32,9				
6-Aminoquinoline	318	357	0,20	0,60				
	277	280	0,61	0,06				
	238	245	1,72	0,70				
	222	—	1,49	0,69				
8-Aminoquinoline	320	335	0,01	0,61				
	295	—	0,26	2,45				
	248	—	0,86	0,04				
	225	—	0,31	4,00				

itself but also as addition of a hydronium cation. From the point of view of the semiempirical computational method that we used, these two cases require the use of different empirical parameters. While the position of the bands in the electronic spectra of the pyridinium and quinolinium cations can be satisfactorily explained by type-I protonation of quinoline and pyridine, a number of molecules of the amino-substituted derivatives, on the other hand, interact via the II type of process. All of the aminopyridines and 2-, 3-, 4-, and 7-aminoquinolines are protonated via the II type of process.

Amino groups in the 2 and 4 positions in pyridine and in the 2, 4, and 7 positions in quinoline, i.e., exactly in those isomers where amine-imine tautomerism is possible, have the greatest effect on the basicity of the heterocycle. The sharply increased basicity of these isomers explains their type-II protonation

in contrast to pyridine and quinoline themselves. However, the fact that the 3-amino derivatives of both pyridine and quinoline are also protonated by a type-II process remains unclear. We have previously shown [5] that acridine, in contrast to pyridine and quinoline, is protonated by a type-II process, which cannot be explained by its basicity. In the case of acridine and the 3-amino derivatives of pyridine and quinoline, protonation of the II type is caused by solvation effects that stabilize the protonated molecules. 5-, 6-, and 8-Aminoquinolines are protonated via a type-I process.

The calculated π-electron density distribution in the molecules of the pyridine and quinoline derivatives satisfactorily explains their chemical properties. For example, the majority of the electrophilic substitution processes in quinoline [7, 8] that proceed in acidic media, occur in the benzene ring. A mixture of 5- and 8-nitroquinolines is formed in the nitration of quinoline, while the 5-nitro derivative is formed in the nitration of ethylquinolinium nitrate. This direction of the electrophilic substitution reactions is in complete agreement with the electron-density distribution in the quinolinium cation but not in the quinoline molecule (Fig. 2).

A different orientation of the substituents is observed in the case of substitution reactions that proceed in neutral or alkaline media. In this case, the electrophilic substituents go primarily into the heteroring in the 3 position. Subsequent substitution occurs in the 6 and 8 positions. In the case of nucleophilic substitution, the 2 position (followed by the 4 position) is the most active. These sorts of directions of substitution reactions in neutral quinoline molecules are in good agreement with the π-electron density distribution and do not require additional assumptions regarding the intermediate formation of 1,2-dihydroquinoline derivatives [7, 13]. Thus, in contrast to the simple MO LCAO method [7], calculations within the Pariser–Parr–Pople variant of the self-consistent-field approximation give electron densities on the atoms, the trends of which for the neutral quinoline molecule and the protonated cation differ. This corresponds to the different directions of substitution reactions in acidic and neutral solutions.

It is known [7] that many reactions of quinoline and its substituted derivatives are in complete agreement with the concept of a fixed, conjugated, diene system of double bonds in the benzene ring. This interpretation of the structure of quinoline, which is based on experimental data, is also in complete accord with the calculated electron-density distribution in the quinoline and aminoquinoline molecules. In all cases, the electron density in the vicinity of the bonds of the 5–6 and 7–8 atoms is almost twice that for other pairs of atoms of the benzene ring.

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