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INTERACTION OF THE ATOMS IN MOLECULES OF PYRIDINE AND ITS DERIVATIVES ACCORDING TO THE RESULTS OF *ab initio* CALCULATIONS

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Nonempirical quantum-chemical calculations of pyridine and its 2-, 3-, and 4-X-substituted derivatives (X = F, Cl, Br, Me, and Et) by RHF/6-311G(d) and MP2/6-311G(d) methods indicate an alternation of charges on the atoms of the pyridine ring and of the occupancy of their valence p_y-orbitals. This is caused by the polarization of bonds under the action of the charges of the atoms geminal to C(n). Bonding molecular orbitals in these molecules, formed as a result of the p_y-orbitals, occurring in the plane of the pyridine ring, are not an indication (characteristic) of p,π-conjugation between the unshared electron pair of the heteroatom of a substituent X and the π-electron system of the ring. The results of the calculations by these methods did not differ in principle.

Keywords: pyridine and its 2-, 3-, and 4-substituted derivatives, charges on atoms, occupancy of atomic orbitals, molecular orbitals, nonempirical quantum chemical calculations, p,π-conjugation.

Quantum-chemical calculations by the RHF/6-31G(d) method have shown [1] that the lower ^{35}Cl NQR frequency of 2-chloropyridine in comparison with the 3- and 4-chloro derivatives is caused by polarization of the C-Cl bond in the former under the direct influence of the partial negative charge of the pyridine ring nitrogen atom. Alternation of the charges on the C atoms in these molecules is also caused by the analogous polarization under the action of the N atom charge. According to existing concepts (see, for example [2,3]) the p-orbital of the N atom in the pyridine molecule (Py, C_5H_5N) and its derivatives (XC_5H_4N), perpendicular to the plane of the pyridine ring, participates in the formation of the π-electron system of the latter, and in the halogen derivatives of pyridine the lone electron pairs of the halogen atom participate in p,π-conjugation with this system. The degree of participation of the halogen atom in such conjugation must be reduced on going from X = F to X = Cl and Br, since the bulk of the halogen atom and of the orbitals of their unshared electron pairs grow in this series and consequently the extent of the overlap of these orbitals with the π-electron system of the ring is reduced.

In the further study of electronic effects in the molecules of pyridine and its 2-, 3-, and 4-substituted derivatives (X = H, F, Cl, Br, Me, and Et) we have carried out quantum-chemical calculations of these molecules with the restricted Hartree-Fock (RHF) method with subsequent estimate of the correlation of electrons within the framework of Möller–Plesset second order perturbation theory (MP2). The 6-311G(d) basis set,

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* Dedicated to Academician of the Russian Academy of Sciences M. G. Voronkov in honor of his 85th birthday.

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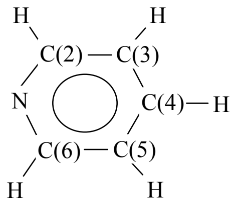
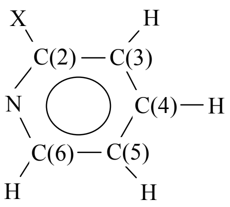
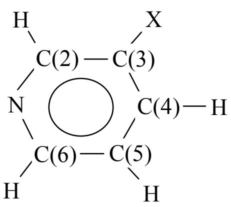
recommended for calculations of molecules, containing atoms of the chemical elements of group III of the Mendeleev periodic table, was used [4]. All the calculations were carried out with full optimization of the geometry of molecules with the GAUSSIAN 94W program [5]. In the calculations of pyridine and its alkyl substituted derivatives the nucleus of the N atom was chosen as the origin of coordinates, and the nucleus of the halogen atom for the halogen derivatives. The Z-axis coincides with the halogen-carbon bond and the Y-axis was perpendicular to the plane of the molecule.


Py


2-XC_5H_4N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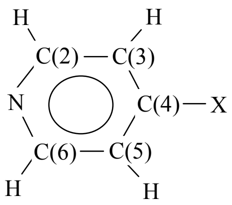
4-XC_5H_4N

According to calculations by both methods the framework of all the studied molecules was planar, i.e. the dihedral angles were 0 or 180°. In the molecules of ethylpyridine both carbon atoms of the ethyl group also lie in the plane of the ring. The dihedral angles CCC(2)N in 2-EtC_5H_4N, CCC(3)C(4) in 3-EtC_5H_4N. and CCC(4)C(3) in 4-EtC_5H_4N were 180°. The axis of symmetry of the p_y-orbitals of the N, C, and halogen atoms was perpendicular to the plane of the molecule. In the molecules of 2-, 3-, and 4-XC_5H_4N calculated by the RHF/6-311G(d) method the bond lengths were somewhat lower, with the exception of the C-X (X = Cl, Br, Me, and Et) bonds, than those calculated by the MP2/6-311G(d) method (Table 1). The results of the calculations of the geometric parameters of pyridine and its derivatives by the latter method were closer to the experimental data, according to which the pyridine bond lengths were N-C(2) 1.340, C(2)-C(3) 1.395, C(3)-C(4) 1.394 Å, and the angles C(2)NC(6) 116.8, NC(2)C(3)123.9, C(2)C(3)C(4) 118.5, and C(3)C(4)C(5) 118.3° [2, 6].

The X-C (X = Cl, Br) bond lengths in 2-XC_5H_4 were a little greater than in the corresponding 3- and 4-substituted derivatives (Table 1). This confirms the results of the calculations carried out previously by the RHF/6-31G(d) method in [1], and is not in agreement with the hypothesis (see for example [3]) on the higher multiplicity of the C-halogen bond in the former molecules in comparison with the latter.

The alternation of the charges on the C atoms in pyridine and its 2- and 3-chloro-substituted derivatives has been noted previously [1]. The present calculations at a higher level confirm this alternation. The same was observed for all the other molecules studied (Table 2). This is caused by the fact that the N atom in them has a significant partial negative charge, under the action of which the electron density of the corresponding C(*n*)X bond is displaced towards the C atom geminal in relation to the C(*n*) atom. As a result the charges on the C(2) and C(6) atoms are usually positive, and on C(4) there is a small negative charge.

In 2-fluoropyridine the strongly electronegative F atom also has a significant negative charge, under the action of which the N and C(3) atoms geminal to C(2) have the greatest negative charges compared with unsubstituted pyridine and its 2-Cl- and 2-Br-substituted derivatives. The direct influence of the negative charges on the N and C(3) atoms through space leads to an increase of the partial negative charge on the C(4) atom in comparison with unsubstituted pyridine and its 2-Cl- and 2-Br-substituted derivatives. Under the direct influence of the significant negative chargeon the F atom in 3-F-pyridine, a small negative charge appears on atom C(2) geminal to atom C(3), but on the other geminal atom C(4) the partial negative charge becomes significant in comparison with unsubstituted pyridine and its 3-Cl- and 3-Br-substituted derivatives. The direct influence of the negatively charged F atom in 4-F-pyridine on the C(3) and C(5) atoms, geminal to C(4), leads to an increase in their partial negative charges compared to unsubstituted pyridine and its Cl and Br substituted derivatives. The significant positive charge on the C atom linked to F in 2-, 3-, and 4-F-substituted pyridines is caused by the F atom.

TABLE 1. Bond Lengths (*d*) in the Molecules of Pyridine and Its 2-, 3-, and 4-Substituted Derivatives (XC_5H_4N), Calculated by the RHF/6-311G(d) and MP2/6-311G(d) Methods.

X	*d*, Å						
	X–C(*n*)	N–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5) –C(6)	C(6)– N
Method RHF/6-311G(d)							
H	—	1.319	1.385	1.382	1.384	1.384	1.320
2-F	1.315	1.292	1.385	1.377	1.390	1.377	1.327
2-Cl	1.744	1.300	1.386	1.379	1.387	1.379	1.324
2-Br	1.903	1.301	1.387	1.380	1.386	1.380	1.324
2-Me	1.506	1.325	1.389	1.383	1.382	1.384	1.317
2-Et	1.514	1.327	1.389	1.385	1.380	1.385	1.316
3-F	1.325	1.317	1.379	1.373	1.383	1.384	1.320
3-Cl	1.740	1.316	1.383	1.379	1.382	1.384	1.319
3-Br	1.895	1.317	1.384	1.380	1.383	1.384	1.319
3-Me	1.508	1.321	1.387	1.389	1.380	1.386	1.316
3-Et	1.517	1.324	1.386	1.391	1.378	1.387	1.314
4-F	1.318	1.320	1.384	1.376	1.376	1.384	1.320
4-Cl	1.737	1.318	1.385	1.379	1.379	1.385	1.318
4-Br	1.894	1.318	1.385	1.380	1.380	1.385	1.318
4-Me	1.507	1.322	1.381	1.390	1.385	1.386	1.317
4-Et	1.516	1.323	1.379	1.393	1.385	1.388	1.315
Method MP2/6-311G(d)							
H	—	1.344	1.398	1.396	1.397	1.398	1.344
2-F	1.341	1.316	1.396	1.392	1.400	1.394	1.348
2-Cl	1.741	1.327	1.399	1.394	1.398	1.395	1.347
2-Br	1.905	1.327	1.400	1.394	1.398	1.395	1.347
2-Me	1.505	1.348	1.402	1.396	1.395	1.398	1.342
2-Et	1.513	1.349	1.401	1.398	1.394	1.398	1.340
3-F	1.343	1.341	1.395	1.389	1.397	1.398	1.344
3-Cl	1.732	1.340	1.399	1.394	1.396	1.397	1.344
3-Br	1.892	1.341	1.400	1.395	1.397	1.397	1.344
3-Me	1.506	1.343	1.402	1.401	1.395	1.398	1.343
3-Et	1.514	1.346	1.402	1.403	1.393	1.399	1.341
4-F	1.342	1.343	1.398	1.389	1.389	1.398	1.343
4-Cl	1.732	1.343	1.398	1.394	1.394	1.398	1.343
4-Br	1.893	1.343	1.398	1.395	1.395	1.398	1.343
4-Me	1.506	1.344	1.396	1.401	1.399	1.398	1.342
4-Et	1.514	1.345	1.395	1.403	1.399	1.400	1.341

The distribution of charges in the studied molecules is therefore subject to the overall rules of the change of electron density on the Y atom in Y-Z-M and Y-Z=M groupings under the influence of the charge on atom M (see for example [1,7, 8]). A negative charge on atom M increases the electron density on atom Y, but a positive decreases it. This is caused by polarization of the Z-Y bond under the direct action of the charge on atom M [1, 7-9].

The charges on atoms in the studied molecules calculated by the RHF and MP2 methods (Table 3) are close to one another, as is the occupancy of the valence *p*-orbitals of the corresponding atoms (Table 4). Since in the basis set 6-311G(d) each valence orbital is represented as the combination of three orbitals of different sizes (see for example [4]), the occupancies given in Table 4 are the sum of three of these components.

In all these molecules alternation occurs of the occupancies of the valence p_y-orbitals of the pyridine ring C atoms. The occupancies of these orbitals is maximal for atoms N, C(3), and C(5), which have the greatest negative charges. In the molecules of 2- and 4-F-pyridine the occupancies of the p_y-orbitals of the N, C(3),

TABLE 2. Valence Angles (α) in Molecules of Pyridine (X = H), and Its 2-, 3-, and 4-Substituted Derivatives (XC_5H_4N)

X	α, deg.						
	C(2)NC(6)	NC(2)C(3)	C(2)C(3)C(4)	C(3)C(4)C(5)	C(4)C(5)C(6)	C(5)C(6)N	XC(*n*)C(*n* + 1)
Method RHF/6-311G(d)							
H	117.71	123.63	118.21	118.61	118.21	123.63	—
2-F	117.09	125.68	116.63	119.24	117.83	123.53	117.92
2-Cl	117.53	124.60	117.08	119.17	117.93	123.46	118.46
2-Br	117.63	124.75	117.08	119.19	117.97	123.38	118.60
2-Me	118.73	121.92	118.99	118.93	117.61	123.81	121.78
2-Et	119.06	121.61	118.96	119.17	117.45	123.76	123.57
3-F	118.44	121.99	120.46	117.19	118.70	123.21	120.15
3-Cl	118.35	122.55	119.42	117.84	118.53	123.31	120.72
3-Br	118.35	122.53	119.41	117.83	118.51	123.38	120.73
3-Me	117.95	124.51	116.56	119.62	118.29	123.07	121.76
3-Et	118.16	124.43	116.28	119.97	118.17	122.98	119.84
4-F	117.51	124.06	116.80	120.76	116.80	124.06	119.62
4-Cl	117.54	123.97	117.35	119.83	117.35	123.97	120.08
4-Br	117.59	123.95	117.38	119.76	117.38	123.95	120.12
4-Me	116.99	123.86	119.21	116.85	119.19	123.89	121.09
4-Et	116.82	123.80	119.54	116.53	119.17	124.13	119.49
Method MP2/6-311G(d)							
H	116.67	123.90	118.67	118.18	118.69	123.88	—
2-F	116.22	126.03	116.96	118.82	118.39	123.59	117.93
2-Cl	116.52	125.06	117.52	118.79	118.39	123.73	118.42
2-Br	116.55	125.12	117.39	118.86	118.42	123.66	118.33
2-Me	117.77	122.25	119.45	118.41	118.23	123.89	121.92
2-Et	118.00	122.06	119.37	118.63	118.10	123.84	123.35
3-F	117.26	122.39	120.75	116.86	119.10	123.65	120.00
3-Cl	117.39	122.87	119.70	117.48	119.06	123.50	120.57
3-Br	117.47	122.76	119.75	117.42	119.09	123.51	120.56
3-Me	116.83	124.82	117.02	119.19	118.72	123.42	121.36
3-Et	117.05	124.65	116.83	119.54	118.55	123.37	123.33
4-F	116.56	124.30	117.23	120.40	117.23	124.30	119.80
4-Cl	116.44	124.30	117.83	119.31	117.83	124.30	120.35
4-Br	116.46	124.34	117.76	119.35	117.76	124.34	120.33
4-Me	116.17	123.98	119.68	116.52	119.67	123.99	121.30
4-Et	116.01	123.90	119.96	116.31	119.57	124.25	119.94

TABLE 3. Charges (q) on Atoms in the Molecules of Pyridine, and Its 2-, 3-, and 4-Substituted Derivatives (XC_5H_4N), Calculated by the RHF/311G(d) and MP2/311G(d)

X	q, e						
	X	N	C(2)	C(3)	C(4)	C(5)	C(6)
			Method RHF/6-311G(d)				
H	—	-0.398	0.031	-0.351	-0.084	-0.351	0.030
2-F	-0.287	-0.414	0.595	-0.441	-0.069	-0.367	0.032
2-Cl	-0.092	-0.397	0.206	-0.287	-0.073	-0.340	0.030
2-Br	-0.030	-0.399	0.164	-0.298	-0.076	-0.346	0.027
2-Me	-0.632	-0.431	0.267	-0.361	-0.075	-0.353	0.027
2-Et	-0.404*	-0.431	0.257	-0.362	-0.069	-0.353	0.028
3-F	-0.310	-0.381	-0.061	0.286	-0.180	-0.333	0.016
3-Cl	-0.096	-0.394	0.103	-0.271	-0.013	-0.347	0.032
3-Br	-0.030	-0.395	0.079	-0.281	-0.036	-0.349	0.036
3-Me	-0.666	-0.398	0.013	-0.107	-0.088	-0.346	0.025
3-Et	-0.441*	-0.406	0.022	-0.107	-0.087	-0.343	0.020
4-F	-0.300	-0.408	0.043	-0.431	0.525	-0.431	0.043
4-Cl	-0.082	-0.399	0.044	-0.292	-0.001	-0.292	0.044
4-Br	-0.016	-0.397	0.044	-0.319	-0.002	-0.319	0.044
4-Me	-0.659	-0.407	0.041	-0.376	0.178	-0.388	0.044
4-Et	-0.433*	-0.406	0.040	-0.372	0.173	-0.393	0.048
			Method MP2/6-311G(d)				
H	—	-0.402	0.026	-0.346	-0.088	-0.346	0.026
2-F	-0.306	-0.417	0.597	-0.425	-0.074	-0.360	0.029
2-Cl	-0.083	-0.400	0.198	-0.285	-0.077	-0.345	0.026
2-Br	-0.022	-0.402	0.156	-0.294	-0.081	-0.341	0.023
2-Me	-0.627	-0.436	0.264	-0.356	-0.080	-0.349	0.024
2-Et	-0.399*	-0.436	0.254	-0.356	-0.074	-0.348	0.025
3-F	-0.323	-0.384	-0.060	0.287	-0.177	-0.328	0.012
3-Cl	-0.090	-0.397	0.094	-0.259	-0.023	-0.340	0.027
3-Br	-0.025	-0.398	0.071	-0.272	-0.045	-0.343	0.031
3-Me	-0.659	-0.402	0.008	-0.098	-0.096	-0.339	0.019
3-Et	-0.434*	-0.410	0.016	-0.098	-0.095	-0.336	0.013
4-F	-0.316	-0.409	0.037	-0.417	0.518	-0.417	0.037
4-Cl	-0.074	-0.402	0.040	-0.290	-0.000	-0.290	0.040
4-Br	-0.009	-0.401	0.039	-0.315	-0.006	-0.315	0.039
4-Me	-0.655	-0.412	0.038	-0.373	0.177	-0.384	0.040
4-Et	-0.427*	-0.411	0.037	-0.369	0.172	-0.388	0.043

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* When X = Me and Et charges are given for C atoms linked with the pyridine ring. Charges for the C atom of the methyl group when X = Et are -0.657, -0.648, and -0.650 e with (RFH), -0.655, -0.646, and -0.649 e (MP2) for 2-, 3-, and 4-substituted derivatives respectively.

and C(5), and in 3-F-pyridine the C(2) and C(4) atoms are greater than in pyridine and its corresponding Cl- and Br-substituted derivatives. Probably such a distribution of p_y-electron density is also caused by the polarization of the corresponding π-bonds of the pyridine ring under the action of the charges on the N and F atoms directly through space.

TABLE 4. Occupancies (N_p) of Valence *p*-Orbitals of the X Atom, and also the p_y-Orbitals of the C and N Atoms in the Molecules of Pyridine, Its 2-, 3-, and 4-Substituted Derivatives (XC_5H_4N), Calculated by the RHF/6-311G(d) and MP2/6-311G(d) Methods

X	X			C(2)	C(3)	C(4)	C(5)	C(6)	N
	Np_x, e	Np_y, e	Np_z, e	Np_y, e	Np_y, e	Np_y, e	Np_y, e	Np_y, e	Np_y, e
Method RHF									
H	—	—	—	0.903	1.029	0.908	1.029	0.904	1.122
2-F	1.940	1.913	1.463	0.867	1.081	0.879	1.060	0.882	1.178
2-Cl	1.980	1.964	1.215	0.952	1.029	0.894	1.031	0.894	1.136
2-Br	2.008	1.988	1.138	0.949	1.023	0.897	1.026	0.897	1.132
2-Me	—	1.148	—	0.863	1.055	0.897	1.048	0.892	1.145
2-Et	—	1.140*	—	0.862	1.056	0.898	1.048	0.891	1.145
3-F	1.944	1.925	1.465	0.958	0.985	0.964	1.001	0.934	1.101
3-Cl	1.967	1.970	1.215	0.902	1.082	0.910	1.016	0.906	1.115
3-Br	2.001	1.995	1.132	0.896	1.079	0.904	1.019	0.902	1.118
3-Me	—	1.127	—	0.931	0.980	0.930	1.020	0.918	1.115
3-Et	—	1.118*	—	0.934	0.977	0.929	1.021	0.917	1.116
4-F	1.945	1.916	1.463	0.877	1.084	0.874	1.084	0.877	1.150
4-Cl	1.967	1.961	1.211	0.890	1.032	0.967	1.032	0.890	1.128
4-Br	2.001	1.987	1.128	0.893	1.026	0.963	1.026	0.893	1.123
4-Me	—	1.135	—	0.897	1.054	0.860	1.058	0.892	1.137
4-Et	—	1.127*	—	0.900	1.054	0.855	1.059	0.892	1.137
Method MP2									
H	—	—	—	0.903	1.031	0.906	1.031	0.903	1.124
2-F	1.943	1.920	1.466	0.873	1.079	0.879	1.058	0.882	1.176
2-Cl	1.976	1.962	1.208	0.952	1.033	0.892	1.035	0.893	1.139
2-Br	2.008	1.988	1.131	0.949	1.026	0.895	1.030	0.896	1.134
2-Me	—	1.145	—	0.862	1.058	0.895	1.051	0.892	1.148
2-Et	—	1.138*	—	0.861	1.058	0.896	1.051	0.891	1.148
3-F	1.945	1.928	1.467	0.954	0.992	0.958	1.005	0.931	1.104
3-Cl	1.966	1.968	1.211	0.904	1.083	0.910	1.018	0.907	1.116
3-Br	2.001	1.994	1.129	0.897	1.080	0.903	1.021	0.902	1.119
3-Me	—	1.125	—	0.931	0.982	0.929	1.022	0.919	1.116
3-Et	—	1.115*	—	0.934	0.978	0.928	1.023	0.918	1.117
4-F	1.947	1.921	1.466	0.878	1.082	0.878	1.082	0.878	1.150
4-Cl	1.966	1.959	1.206	0.890	1.036	0.964	1.036	0.890	1.131
4-Br	2.002	1.985	1.122	0.892	1.030	0.960	1.030	0.892	1.126
4-Me	—	1.133	—	0.896	1.057	0.858	1.060	0.893	1.140
4-Et	—	1.126*	—	0.899	1.057	0.853	1.061	0.893	1.140

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* Occupancies of the p_y-orbital of the C atom of the methylene group. Occupancies of this orbital of the methyl group C atom were 1.110, 1.118, and 1.117 e (RHF), 1.107, 1.114, and 1.113 e (MP2) in 2-, 3-, and 4-ethyl-substituted derivatives of pyridine respectively.

The occupancies of the p_y-orbitals of the halogen atoms directed perpendicular to the plane of the pyridine ring are lower than the p_x-orbitals lying in the plane of the ring (the exception is the occupancy of the p_y-orbitals of the Cl atom in 3-Cl-pyridine). Theoretically this may be explained by the participation

TABLE 5. Energies (-*E*) of the Bonding Molecular Orbitals Formed by the Atomic p_y-Orbitals and Coefficients (κ) on the Latter in the Molecules of Pyridine, Its 2-, 3-, and 4-Substituted Derivatives (XC_5H_4N), Calculated by the RHF/6-311G(d) and MP2/6-311G(d) Methods

X	–*E*, eV	κ						
		X	C(2)	C(3)	C(4)	C(5)	C(6)	N
Method RHF								
H	14.842	0.000	0.388	0.305	0.283	0.305	0.388	0.513
2-F	19.273	1.058	0.318	0.097	0.038	0.027	0.055	0.152
2-Cl	15.954	0.328	0.473	0.282	0.223	0.221	0.313	0.486
2-Br	15.756	0.200	0.457	0.295	0.242	0.249	0.341	0.511
2-Me	15.994	0.591	0.311	0.179	0.118	0.108	0.167	0.295
2-Et	16.929	0.521*	0.192	0.104	0.053	0.042	0.073	0.153
3-F	19.297	1.090	0.091	0.291	0.086	0.034	0.024	0.050
3-Cl	15.736	0.346	0.362	0.415	0.283	0.258	0.299	0.421
3-Br	15.556	0.195	0.383	0.384	0.292	0.280	0.383	0.462
3-Me	16.052	0.632	0.182	0.263	0.165	0.106	0.109	0.162
3-Et	17.070	0.533*	0.098	0.164	0.085	0.042	0.039	0.066
4-F	19.495	1.093	0.034	0.086	0.285	0.086	0.034	0.027
4-Cl	15.702	0.490	0.318	0.304	0.402	0.304	0.318	0.391
4-Br	15.515	0.201	0.353	0.315	0.366	0.315	0.353	0.448
4-Me	16.142	0.651	0.111	0.162	0.245	0.153	0.112	0.120
4-Et	17.177	0.540*	0.044	0.087	0.154	0.089	0.047	0.043
Method MP2								
H	14.612	—	0.388	0.312	0.291	0.312	0.388	0.506
2-F	19.029	1.069	0.309	0.095	0.038	0.026	0.052	0.144
2-Cl	15.733	0.366	0.475	0.284	0.223	0.218	0.305	0.473
2-Br	15.505	0.218	0.459	0.300	0.248	0.252	0.339	0.503
2-Me	15.893	0.606	0.301	0.171	0.109	0.097	0.151	0.273
2-Et	16.876	0.522*	0.185	0.100	0.049	0.037	0.064	0.141
3-F	19.141	1.097	0.086	0.285	0.083	0.032	0.021	0.046
3-Cl	15.544	0.399	0.353	0.427	0.258	0.254	0.284	0.398
3-Br	15.324	0.219	0.380	0.395	0.298	0.283	0.332	0.452
3-Me	15.987	0.644	0.168	0.258	0.158	0.095	0.093	0.141
3-Et	17.027	0.532*	0.094	0.163	0.086	0.039	0.035	0.059
4-F	19.296	1.101	0.032	0.082	0.279	0.082	0.032	0.025
4-Cl	15.520	0.427	0.302	0.303	0.416	0.303	0.302	0.362
4-Br	15.284	0.227	0.348	0.321	0.379	0.321	0.348	0.434
4-Me	16.083	0.661	0.098	0.154	0.241	0.144	0.099	0.101
4-Et	17.136	0.539*	0.040	0.084	0.153	0.086	0.043	0.037

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* Coefficients on p_y-orbitals of the C atom bound to the pyridine ring. These values for the C atom of the methyl group are 0.425, 0.429, and 0.430 (RHF), 0.431, 0.432, and 0.432 (MP2) in 2-, 3-, and 4-EtPy respectively.

of the p_y-orbitals of the halogen atoms in p,π-conjugation with the π-electron system of the ring. In 2- and 4-halo-substituted pyridine on going from X = F to X = Cl and Br the occupancy of the p_y-orbitals of the N, C(2), and C(4) atoms is reduced, but increases in 3-substituted derivatives. The occupancy of the p_y-orbitals of the halogen atoms also increases in the same transition.

This might have been explained by a reduction in the ability of the unshared pairs of electrons of the latter to participate in p,π-conjugation on increasing the size of the p_y-orbital of the halogen atom compared with the analogous orbitals of the ring C atoms. However the same growth is also observed for the p_x-orbitals of the halogen atoms not capable of such conjugation. Consequently this must be explained by completely different reasons. The reduction in occupancy of the p_z-orbitala of the halogen atoms on going from X = F to X = Cl and Br corresponds to the ratio of the electronegativities of the latter [10].

It may be assumed that the π-bonding molecular orbital in the substituted pyridine derivatives, formed by the atomic p_y-orbitals directed perpendicular to the plane of the pyridine ring, is the result of p,π-conjugation between the unshared electron pair of the heteroatom X and its π-electron system. The energies of such molecular orbitals are given in Table 5, as are the coefficients at the atomic p_y-orbitals forming them. These coefficients are the sum of the coefficients on the three component atomic orbitals. However such a bonding molecular orbital is also formed with the participation of the p_y-orbitals of the sp^3-hybridized C atoms occurring in the plane of the pyridine ring and not capable of such conjugation (including the atoms not bound to the pyridine ring in X = Et). Consequently, the bonding molecular orbitals in pyridine and its derivatives, formed as a result of the p_y-orbitals of the atoms occurring in the plane of the pyridine ring, are not an indication (characteristic) of p,π-conjugation between the unshared pair of electrons of the heteroatom X and the π-electron system of the ring.

In pyridine the greatest contribution to the bonding molecular orbital is from the p_y-orbital of the N atom, and in 2-, 3-, and 4-fluoropyridines from the p_y-orbital of the F atom. The contributions from the N and C atoms in the latter are insignificant. The exceptions are the contributions from the C atoms to which the F atom is bound. On going from X = F to X = Cl and Br the contribution from the halogen atom is reduced and from the N atom is increased. This is in agreement with the reduction in the ability of the p_y-orbitals of the halogen atom to participate in the interaction of the π-electron system of the ring in such a transition owing to the increase in bulk of this orbital, and also with the larger contribution from the C atoms of the methyl and ethyl groups to the bonding molecular orbital, than from the Cl and Br atoms. The results of the calculations by the RHF and MP2 methods do not differ in principle (Table 5).

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REFERENCES

1. V. P. Feshin and M. Yu. Kon'shin, *Izv. Akad. Nauk, Ser. Khim.*, 2641 (1996).
2. O. Ya. Neiland, *Organic Chemistry* [in Russian], Vyssh. Shkol., Moscow (1970), 751 pp.
3. M. J. S. Dewar and E. A. C. Lucken, *J. Chem. Soc.*, 2653 (1958).
4. J. B. Foresman and A. E. Frisch, *Exploring Chemistry with Electronic Structure Methods*, 2nd ed., Gaussian, Pittsburgh (1996), 302 pp.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94, Revision E. 3*, Gaussian, Pittsburgh (1995).

6. D. M. Smith, *Pyridines,* in I. K. Kochetkov (editor), *Comprehensive Organic Chemistry*, Vol. 8 [in Russian], Khimiya, Moscow (1985), p. 15.
7. V. P. Feshin, *Electronic Effects in Organic and Heteroorganic Molecules* [in Russian], Urals Branch of the Russian Academy of Sciences, Ekaterinburg (1997), 377 pp.
8. V. P. Feshin, *Zh. Org. Khim.*, **74**, 1929 (2004).
9. V. P. Feshin, M. G. Voronkov, and L. S. Romanenko, *Dokl. Akad. Nauk*, **256**, 1431 (1981).
10. L. Pauling, *General Chemistry* [Russian translation], Mir, Moscow (1974), 864 pp.