Ab initio calculations of pyridine and its 2- and 3-chloroderivatives

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Ab initio calculations of the C_5H_5N, 2-, and 3-ClC_5H_4N molecules by the RHF method in the valence split 6-31G* basis set with full optimization of the geometry have been carried out. The alternation of the charges on the atoms of the pyridine ring and of the populations of their p_x-orbitals is in agreement with the noninductive through-the-field interaction of the geminal atoms. The ^{35}Cl NQR frequencies and the electric field gradient asymmetry parameters at the ^{35}Cl nuclei in 2- and 3-ClC_5H_4N were estimated using the populations of the valent p-orbitals of the Cl atoms and their components. The ^{35}Cl NQR frequency for the first compound is lower than that for the second one, mainly due to the higher p_σ-electron population of its Cl atom.

Key words: *ab initio* calculations; pyridine, 2- and 3-chloropyridines; population of the p-orbital; ^{35}Cl NQR frequency, asymmetry parameter.

An analysis of the ^{35}Cl NQR spectra of nitrogen-containing heterocyclic compounds shows that the NQR frequency of the chlorine atom nucleus in the α-position to the nitrogen atom in the nitrogen-containing heterocyclic compounds is always lower than that for the chlorine atoms in other positions of the cycle.[1] Thus, the ^{35}Cl NQR frequency of 2-chloropyridine (34.194 MHz) is lower than that of 3-chloropyridine (35.238 MHz) and 4-chloropyridine (34.89 MHz), whereas for 2-chloroquinoline (33.271 MHz) it is much lower than for 6-chloroquinoline (34.628 MHz). The average value of the NQR frequency of the chlorine atomic nucleus in the α-position of 4,5-dichloropyrimidine (35.845 MHz) is ~1.6 MHz lower than that of the β-chlorine atom (37.431 MHz). The ^{35}Cl NQR frequency in 1-methyl-4-chloroimidazole (35.034 MHz) is appreciably lower than that in 1-methyl-5-chloroimidazole (36.822 MHz), *etc.*[1,2]

The NQR frequencies for the α-chlorine atoms in chlorosubstituted pyridine, quinoline, 2-substituted 6-chloro-7-azaindole *etc.* are lower, and those for β- and γ-chlorine atoms are higher than those in the corresponding derivatives of chlorobenzene, chloronaphthalene, *etc.*[1,2] The NQR frequencies for the β- and γ-chlorine atoms in these heterocyclic compounds reflect the induction effect of the N atom, which is more electronegative than the carbon atom. At the same time, the ^{35}Cl NQR frequencies of the α- chlorine atoms of the above compounds are not compatible with such an effect.

It is assumed that the induction effect of the N atoms on the α-chlorine atom in nitrogen-containing heterocyclic compounds is offset by a shift of the unshared electron pair of that Cl atom towards the C—Cl bond which increases its multiplicity and decreases the ^{35}Cl NQR frequency.[2–4] The noninduction character of the effect of a heteroatom M (N, O, F, Si, Ge, Sn, P, *etc.*) is also observed in other organic and organoelement compounds where the indicator atom Y is in the α-position to the heteroatom M (in structures with linear triatomic groups Y—Z—M, Y—C=M, Y—Z=M, *etc.*).[1,5–7] In the framework of the classic concept of electron shifts this is explained by various conjugation effects depending on the nature of the Y, Z, and M atoms.[1,2,5–7]

An analysis of all of the experimental results of studying the noninduction effect of the M atom on the Y atom in such compounds showed that the effect is caused by the same mechanism of the interaction of geminal Y and M atoms for any Y, Z, and M: the polarization of the C—Y (Z—Y) bond due to the direct action of the M atom through the field.[1,5–7] No allowance for such interaction is made when the induction constants of substituents containing a heteroatom M are estimated.[8] For a further study of the nature of the interaction between atoms in molecules containing a nonlinear group Y—C—M (Y—C=M) we performed *ab initio* calculations of pyridine (**1**) as well as of 2- (**2**), and 3-chloropyridine (**3**) molecules with full optimization of their geometry.

The calculations were carried out by the restricted Hartree—Fock method in the valence split 6-31G* basis set using the GAUSSIAN-92 for Windows program (Gaussian, Inc.).[9] For pyridine, the origin was chosen at the H(1) nucleus, and the origin for 2- and 3-ClC_5H_4N was at the Cl(1) nucleus. The *z*-axis for the first molecule is directed along the H(1)—C(2) bond, while for the two other molecules it is directed along the Cl(1)—C(2)

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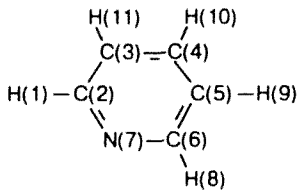

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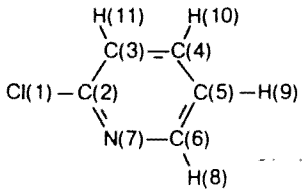

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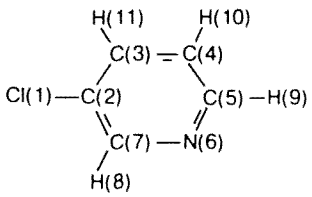

3

bond. For all molecules, the x axis is perpendicular to the molecular plane. Several results of calculations of the chlorobenzene* molecule carried out by the RHF/6-31C* method are also given for comparison.

The optimized geometric parameters of molecules **1**, **2**, and **3** are listed in Table 1, the Mulliken charges on the atoms of these molecules and on those of chlorobenzene are given in Table 2, and the populations of the valent p-orbitals of their C, N, and Cl atoms are presented in Table 3. Along with the total population, the populations of both the less diffuse components (2p for the C and N atoms, and 3p for the Cl atom) and the more diffuse components (3p for the C and N atoms, and 4p for the Cl atom) of the valent p-orbitals of the C, N, and Cl atoms in the valence split basis set are given.

Results and Discussion

According to calculations, molecules **1**, **2**, and **3** are planar: all their dihedral angles are equal to 0 or 180°. Such a geometry is favorable for participation of the N and Cl atoms in p,π-conjugation with the π-electron system of the molecule: the p_x-orbitals of these atoms are perpendicular to the molecular plane. The lengths of the corresponding bonds of these compounds differ only in the third digit.

The C—Cl bond in molecule **2**, for which an increase in multiplicity is assumed to explain the abnormally low ^{35}Cl NQR frequency (see above), is even somewhat longer than that in isomer **3**; the value of the ^{35}Cl NQR frequency in **3** can be explained by the induction effect of the N atom on the Cl atom. According to *ab initio* calculations, the C—Cl bond in both these molecules is somewhat shorter than in C_6H_5Cl (1.753 Å). However, this does not mean that the order of the C—Cl bonds in these compounds is different, since the total populations of the p_x-orbitals of the Cl atoms are nearly the same (see Table 3).

The N atoms in molecules **1**, **2**, and **3** have the largest negative charges, while the Cl atoms in molecules **2** and **3** are slightly positive. At the same time, the Cl atom in chlorobenzene has a small negative charge (see Table 2). In all studied molecules, the C atoms bonded to the N atoms are positively charged, whereas in C_6H_5Cl the charges on all C atoms are negative and successively increase as the distance between the C atoms and Cl atom increases. In pyridine and its chloroderivatives the carbon atoms in the geminal positions to the N atoms have the largest negative charges.

This is in accordance with the direct through-the-field polarization of the C—C bonds by the large nega-

Table 1. Bond lengths (d) and bond angles (ω) in molecules **1**, **2**, and **3**

	1	**2**	**3**
Bond		d/Å	
Cl(1)—C(2)	—	1.742	1.738
C(2)—C(3)	1.385	1.387	1.380
C(3)—C(4)	1.384	1.380	1.383
C(4)—C(5)	1.384	1.387	1.384
C(5)—C(6)	1.385	1.380	—
C(6)—N(7)	1.320	1.325	—
C(6)—H(8)	1.076	1.075	—
C(5)—H(9)	1.074	1.740	1.075
C(4)—H(10)	1.075	1.075	1.074
C(3)—H(11)	1.074	1.072	1.074
C(5)—N(6)	—	—	1.320
N(6)—C(7)	—	—	1.318
C(7)—H(8)	1.076	—	1.074
Angle		ω/deg	
Cl(1)—C(2)—C(3)	—	118.6	120.7
C(2)—C(3)—C(4)	118.2	117.1	117.8
C(3)—C(4)—C(5)	118.6	119.2	118.6
C(4)—C(5)—C(6)	118.2	118.0	—
C(5)—C(6)—N(7)	123.6	123.4	—
C(5)—C(6)—H(8)	120.3	120.8	—
C(4)—C(5)—H(9)	121.4	121.5	120.5
C(3)—C(4)—H(10)	120.7	120.1	120.9
C(2)—C(3)—H(11)	120.4	120.7	120.6
C(4)—C(5)—N(6)	—	—	123.4
C(5)—N(6)—C(7)	—	—	118.4
N(6)—C(7)—H(8)	120.3	—	117.2

Table 2. Charges on the atoms (q/e) in molecules **1**, **2**, **3**, and C_6H_5Cl (**4**)

Molecule	Cl(1)	C(2)	C(3)	C(4)	C(5)	C(6,7)	N
1	—	0.067	−0.257	−0.143	−0.257	0.067	−0.516
2	0.008	0.147	−0.226	−0.136	−0.258	0.068	−0.503
3	0.011	−0.192	−0.122	−0.251	−0.068	0.092	−0.508
4	−0.008	−0.132	−0.182	−0.193	−0.201	—	—

* More detailed results of this calculation are published elsewhere.

Table 3. The populations (ΣN_p) of the valent p-orbitals of the C, N, and Cl atoms in molecules **1**, **2**, and **3** and their components (2p, 3p, 4p), ^{35}Cl NQR frequencies (ν_p) and the EFG asymmetry parameters at the ^{35}Cl nuclei (η_p) calculated using these populations

Molecule	Atomic orbital	Cl					C(2)	C(3)	C(4)	C(5)	C(6, 7)	N
		N_x	N_y	N_z	ν_{calc}/MHz	η_{calc} (%)	N_x	N_x	N_x	N_x	N_x	N_x
1	2p						0.494	0.539	0.484	0.539	0.494	0.618
	3p						0.405	0.494	0.431	0.494	0.405	0.528
	ΣN_p						0.899	1.033	0.915	1.033	0.899	1.146
2	2p						0.545	0.551	0.479	0.542	0.492	0.637
	3p	1.298	1.324	0.948	33.883	10.91	0.400	0.483	0.423	0.493	0.398	0.523
	4p	0.652	0.639	0.185	61.335	4.43	—	—	—	—	—	—
	ΣN_p	1.950	1.963	1.133	45.124	2.37	0.945	1.034	0.902	1.035	0.890	1.160
3	2p						0.592	0.496	0.534	0.498	0.506	0.615
	3p	1.307	1.317	0.940	34.683	4.13	0.487	0.423	0.484	0.405	0.395	0.522
	4p	0.651	0.646	0.181	62.191	1.56	—	—	—	—	—	—
	ΣN_p	1.958	1.963	1.121	46.001	0.89	1.079	0.919	1.018	0.903	0.901	1.137

tive charge on the N atom geminal to these bonds (like in other molecules containing Y—C—M (Y—C=M) group with a partially negatively charged M atom (see above). As the distance between the C atoms of the pyridine ring and the electronegative N and Cl atoms increase due to a weakening of the induction effect of the latter, the negative charges on the C atoms must increase like those in chlorobenzene. Accordingly, the charges on the C(4) atoms in molecules **1** and **2** should be the most negative.

However, the C(4) atoms in the compounds in question have the smallest negative charges because of polarization of the C(3)—C(4) and C(4)—C(5) bonds due to the direct through-the-field effect of the positively charged geminal C(2) and C(6) atoms, respectively. The same is true for the C(3) atom in molecule **3**. An analogous decrease in the electron population of the Y atom occurs under the action of the positively charged M atom in the Y—C—M group (M = Si, Ge, Sn, P, *etc.*).[1,5–7] If a C atom in the benzene ring is replaced by an electronegative N atom, *i.e.*, on going from C_6H_5Cl to compound **3**, the p_σ-electron population of the Cl atom decreases (the population of its p_z-orbital decreases) (see Table 3 and 4), whereas the populations of its p_x- and p_y-orbitals remain nearly the same, and are almost as electronodeficient as in C_6H_5Cl.

The p_σ-electron population of the Cl atom increases on going from isomer **3** to isomer **2** despite the closer approach of the Cl atom to the strong electron-acceptor N atom. In accordance with the induction effect of the latter this should decrease the p_σ-electron population of the Cl atom. However, in this case, favorable conditions for polarization of the C—Cl bond due to the direct through-the-field effect of the negatively charged N atom are created (as in other compounds containing a Cl—C—M (Cl—C=M) group (see above)). This polarization is superior to the induction effect of the geminal N atom. In this case the population of the p_y-orbital of the Cl atom does not change, whereas the population of the p_x-orbital decreases very slightly (see Table 3).

In molecules **1**, **2** and **3**, the p_x-orbitals of the N atoms are electron-excessive, *i.e.*, their populations exceed unity. In this case the excess of the p_x-electrons on the N atom in molecule **2** is greater than that in **1** and **3** in accordance with the direct through-the-field polarization of the C(2)—N(7) bond due to the effect of the geminal chlorine atom in molecule **2**. In all these molecules, the populations of the p_x-orbitals of the C atoms alternate: those, adjacent to the N atom are electron-deficient, and those in the geminal positions are electron-excessive; the C atom in position 4 of the pyridine ring is also electron-deficient, however, to a lesser degree than the C atoms that are geminal to the N atom. This alternation is in agreement with the noninduction interaction between the geminal N and C atoms in the pyridine ring, as well as with the "abnormal" relationships of changes in the electron population of the Y atom in the Y—C—M (or Y—C=M) group due to the direct through-the-field effect of the charge of the M atom and transmission of this effect along the atom chain.[10]

Recently, the NQR frequencies and the asymmetry parameters of the electric field gradient (EFG) at the nucleus of the indicator atom have been shown[11–14] to characterize the electron density of its valent atomic p-orbitals not in the whole space, as accepted in the Townes—Dailey theory (see, for instance, Refs. 2, 15,

Table 4. The populations (ΣN_p) of the valent p-orbitals of the Cl and C atoms in the C_6H_5Cl molecule and their components (N_p)

Atomic orbital	Cl			C(2,6)	C(3,5)	C(4)
	N_{px}	N_{py}	N_{pz}	N_{px}	N_{px}	N_{px}
3p	1.303	1.316	0.946	—	—	—
4p	0.656	0650	0.191	—	—	—
ΣN_p	1.959	1.966	1.137	1.039	0.994	0.976

16), but only in the vicinity of the atomic nucleus. The more diffuse part of the valent p-electron shell of the atom contributes only slightly to those values.

The ^{35}Cl NQR frequencies calculated using Eq. (1) with full populations of the valent p-orbitals of the Cl atoms in molecules **2** and **3** (see Table 3) appreciably differ from the experimental values (see above); the same is also observed in other chlorine containing compounds.[11—14] At the same time, the ^{35}Cl NQR frequencies of these molecules calculated using only the populations of the less diffuse 3p-components of the valent p-orbitals of the Cl atoms (see Table 3) are close to the experimental values. The ^{35}Cl NQR frequency of molecule **2** is lower than that of molecule **3** mainly due to the higher p_σ-electron population of the Cl atom (the population of the p_z-orbital), since the half-sums of the populations of the 3p-components of the p_x- and p_y-orbitals of the Cl atoms in these two molecules are nearly equal. This is in agreement with the explanation given for the ^{35}Cl NQR frequency in α-chloropyridine, which is lower than those in the β- and γ-isomers; it is assumed that the C—Cl bond in α-chloropyridine is polarized due to a direct through-the-field effect of the negatively charged N atom.

$$\nu = (e^2Qq_{atom}/2h)[(N_{px} + N_{py})/2 - N_{pz}](1 + \eta^{2/3})^{1/2}, \quad (1)$$

$$\eta = |3(N_{px} - N_{py})/(2N_{pz} - N_{px} - N_{py})|. \quad (2)$$

The EFG asymmetry parameters at the ^{35}Cl nuclei in molecules **2** and **3** were not measured experimentally. However, these values can be estimated using Eq. (2) and the populations of the valent p-orbitals of the Cl atoms.[2,15—17] The asymmetry parameters calculated using the populations of the less diffuse 3p-components of the valent p-orbitals of chlorine atoms obtained from the *ab initio* calculations of the corresponding molecules in the 6-31G* basis set are usually close to the experimental values.[11—14] However, they differ appreciably from the experimental values (as well as the ^{35}Cl NQR frequencies)[11—14] if full populations of these orbitals are used in the calculations.

The values of h for isomers **2** and **3** (as well as for other chlorine-containing molecules) estimated using the full populations of the valent p-orbitals of the chlorine atoms are close to zero, but they differ appreciably from zero if only the less diffuse 3p-components are used. In this case the value of h for molecule **2** is much larger than that for **3** which can not be explained by an increase in the multiplicity of the C—Cl bond in the first structure, since the full populations of the p_x-orbitals of their chlorine atoms are nearly the same (see Table 3). The asymmetry parameter for molecule **2** is larger than that for **3** manly due to the much larger difference between the populations of the 3p-components of the valent p_x- and p_y-orbitals of the Cl atom in the first molecule.

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