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FEATURES OF ATOMIC INTERACTION IN THE MOLECULES OF FURAN, PYRROLE, AND THEIR 2-CHLORINE-SUBSTITUTED DERIVATIVES ACCORDING TO RESULTS OF *ab initio* CALCULATIONS

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The results of ab initio studies by the RHF/6-31G(d) method on the molecules of furan, pyrrole, and their 2-chlorine-substituted derivatives with full optimization of the geometry show that unshared electron pairs of their heteroatoms are not delocalized solely in the π-system of the heterocycle. The participation of these electron pairs in formation of bonding and other MOs does not make it possible to speak of substantial role for p,π-conjugation in the distribution of electron density in the molecules and its effect on the characteristics of the compounds. The results of the ab initio calculations were used to determine the ^{35}Cl NQR parameters of the 2-chlorine-substituted molecules.

According to theories about the polarization of the C–Cl bond in the Cl–C–M or Cl–C=M group under the influence of the charge of atom M directly through the field, a more electronegative (more negatively charged) atom M increases the $p\sigma$-electron density at the chlorine atom, while a less electronegative (less negatively charged) atom reduces it (e.g., see [1]). The ^{35}Cl NQR frequencies of compounds containing such groups are in accordance with this relationship. For example, the ^{35}Cl NQR frequencies in derivatives of the $ClCH_2OR$ (M = O) series, the oxygen atom of which has a significant negative charge, are substantially lower than in alkyl chlorides (M = C), while in compounds of the $ClCH_2MXX'X''$ (M = Si, Ge, Sn) series they are higher than in the organic analogs as a result of the high positive charge of the M atom in the heteroorganic molecules. The ^{35}Cl NQR frequencies of the carboxylic acid chlorides RCOCl (M = O) are much lower than those of compounds of the RCl series (M = C). The NQR frequency of 2-chloropyridine (M = N) is significantly higher than that of 3- and 4-chloropyridine and chlorobenzene (M = C), while that of 2-chlorothiophene (M = S) conversely is higher than that of chlorobenzene, and so forth (e.g., see [1]).

The noninduction effect of the heteroatom M on the $p\sigma$-electron density of the chlorine atom is confirmed by the *ab initio* calculations of molecules containing the Cl–C–M and Cl–C=M groups [1-4]. The ^{35}Cl NQR frequencies of a large number of chlorine-containing organic and heteroorganic compounds (including those mentioned above), calculated from the population densities of the 3*p*-constituents of the valence *p*-orbitals of the chlorine atoms [Eq. (1)] obtained by the RHF/6-31G(d) method, are usually close to the experimental values and correlate with them satisfactorily [Eq. (2)] [1,6].

$$\nu = (e^2Qq_{\mathrm{at}}/2\mathrm{h})[(\mathrm{N}_{px} + \mathrm{N}_{py})/2 - \mathrm{N}_{pz}](1 + \eta^{2/3})^{1/2}; \qquad (1)$$

$$\nu_{\mathrm{B}}(\mathrm{N}_{3p}) = 1.028(\pm 0,041)\nu_e - 1.155(\pm 1.334),\ r = 0.996,\ n = 23 \qquad (2)$$

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Similar agreement and correlation are observed for the asymmetry parameters (η) of the electric field gradient (EFG) at the ^{35}Cl nuclei [1, 6]:

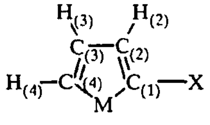
$$\eta_B(\%) = 0.423 + 0.998\eta_e,\ r = 0.968,\ n = 7 \tag{3}$$

This makes it possible to judge from the experimental values ν_e and η_e the accuracy of the quantum-chemical calculations of the electron distributions in the chlorine-containing molecules and, conversely, to determine the ^{35}Cl NQR parameters in terms of the RHF/6-31G(d) method.

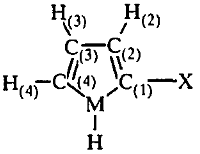
Earlier, thiophene and 2-chlorothiophene were studied by the ^{35}Cl NQR and ab initio methods [4, 7]. Good agreement was achieved between the mean value of the experimental NQR frequencies of 2-chlorothiophene (ν_{av} = 36.961 MHz) and the frequency calculated by the population densities of the 3*p*-constituent of the valence *p*-orbitals of the chlorine atom (ν_B = 36.477 MHz). The higher ^{35}NQR frequency of 2-chlorothiophene compared with that of chlorobenzene was shown to be due mainly to the lower *p*σ-electron density of the chlorine atom in the first molecule.

Other 2-chlorine-substituted five-membered heterocyclic compounds (2-chlorofuran and its derivatives) cannot usually be crystallized. Their ^{35}Cl NQR spectra have not therefore been obtained. An experimental NQR spectrum of 2-chloropyrrole is not available also. These spectra are of interest from the standpoint of the noninduction effect of the oxygen and nitrogen atoms correspondingly on the geminal chlorine atom.

In this connection we have performed *ab initio* calculations by the Hartree – Fock method in the 6-31G(d) split valence basis set with full optimization of the geometry of the molecules (Ia and IIa respectively), and this made it possible to calculate their ^{35}Cl NQR parameters. The furan and pyrrole molecules (I and II respectively) were also calculated similarly by the Gaussian 92 software [8] in order to study features of the electron distribution in five-membered heterocyclic compounds. The origin of the coordinates here was taken as the point where the nucleus of the chlorine atom is located. The *z* axis was directed along the Cl–C bond, and the *y* axis was perpendicular to the plane of the molecule.



M = O, I X = H, Ia X = Cl



M = N, II X = H, IIa X = Cl

According to the results from optimization of the geometry, all the investigated structures are planar [all the calculated dihedral angles are 0° or 180° (±0.02° for I, Ia, and IIa and ±0.08° for II)]. In the molecules of II and IIa all three nitrogen atoms lie almost in one plane (dihedral angles $HNC_{(2)}C_{(3)}$ 180.04° and 180.01° respectively). The bond lengths and bond angles in these molecules are given in Table 1.

The population densities of the valence *p*-orbitals of the chlorine atoms and also their components in the derivatives Ia and IIa are given in Table 2. These populations were used to calculate the ^{35}Cl NQR frequencies and the asymmetry parameters of the electric field gradient at the ^{35}Cl nuclei. As already mentioned, satisfactory agreement with the experimental NQR parameters can be obtained if the population densities of the less diffuse 3*p*-constituents of the valence *p*-orbitals of the chlorine atom in the extended 6-31G(d) basis set are used for the calculations. It can be supposed that the ν_B and η_B values for the molecules of Ia and IIa obtained in this way are close to the actual values.

According to the *ab initio* calculations, the negative charge at the nitrogen atom in IIa is higher than at the oxygen atom in Ia (Table 3). Accordingly, a lower NQR frequency must be expected for IIa than for Ia, and this is confirmed by the results of the corresponding calculations from the population densities of the valence *p*-orbitals and their components for the chlorine atoms. The sulfur atom in 2-chlorothiophene is positively charged [4], and the ^{35}Cl NQR frequencies are therefore higher [7] than in compounds Ia and IIa.

TABLE 1. The Bond Lengths (*d*) and Bond Angles (φ) in the Molecules of Compounds I, Ia, II, IIa

Bond	*d*, Å		Angle	φ, deg.	
	I	II		I	II
C–M	1,344	1,363	$C_{(1)}MC_{(4)}$	107,1	109,5
$C_{(1)}$–$C_{(2)}$	1,339	1,358	$MC_{(1)}C_{(2)}$	110,8	108,2
$C_{(2)}$–$C_{(3)}$	1,441	1,427	$C_{(1)}C_{(2)}C_{(3)}$	105,6	107,1
C–H	~1,07	~1,07	$H_{(1)}C_{(1)}M$	116,1	121,1
N–H	—	0,992	$C_{(1)}C_{(2)}H_{(2)}$	126,8	126,0
			$C_{(2)}C_{(3)}H_{(3)}$	127,6	126,9
			$C_{(3)}C_{(4)}H_{(4)}$	133,0	130,8
			$C_{(1)}NH$		125,3
Bond	Ia	IIa	Angle	Ia	IIa
Cl–$C_{(1)}$	1,706	1,719	$ClC_{(1)}M$	116,5	120,3
$C_{(1)}$–M	1,333	1,357	$C_{(1)}MC_{(4)}$	106,6	108,6
M–$C_{(4)}$	1,350	1,366	$MC_{(4)}C_{(3)}$	110,6	108,2
$C_{(4)}$–$C_{(3)}$	1,337	1,356	$C_{(4)}C_{(3)}C_{(2)}$	106,0	107,5
$C_{(3)}$–$C_{(2)}$	1,442	1,428	$C_{(1)}C_{(2)}H_{(2)}$	126,8	126,1
C–H	~1,07	~1,07	$C_{(2)}C_{(3)}H_{(3)}$	127,2	126,4
N–H	—	0,993	$C_{(3)}C_{(4)}H_{(4)}$	133,6	131,0
			$C_{(1)}NH$	—	125,0

TABLE 2. The Population Densities of the *p*-Orbitals of the Chlorine Atoms (Σ*Np*) and Their 3*p*- and 4*p*-Constituents in the Molecules of Ia and IIa and also the ^{35}Cl NQR Frequencies (ν_B) and Asymmetry Parameters of the Electric Field Gradient at the ^{35}Cl Nuclei (η_B) Calculated from Them

Molecule	Orbital	N_{p_x}, e	N_{p_y}, e	N_{p_z}, e	ν_B, MHz	η_B, %
Ia	3*p*	1,325	1,314	0,931	36,18	4,20
	4*p*	0,630	0,640	0,162	63,04	3,00
	Σ*Np*	1,955	1,954	1,093	47,22	0,25
IIa	3*p*	1,215	1,314	0,939	34,94	0,50
	4*p*	0,643	0,648	0,174	62,82	1,43
	Σ*Np*	1,958	1,962	1,113	46,41	0,57

TABLE 3. The Charges (*q*) at the Atoms in the Molecules of Compounds I, Ia, II, IIa

Molecule	X	M	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
I*	0,217	-0,532	0,112	-0,276	-0,276	0,113
I*[2]	0,221	-0,547	0,109	-0,271	-0,271	0,109
II*	0,203	-0,703	0,026	-0,265	-0,265	0,026
Ia*	0,051	-0,525	0,205	-0,256	-0,266	0,106
IIa*	0,021	-0,709	0,124	-0,248	-0,263	0,031

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* RHF/6-31G(d) method.

*[2] RMP 2/6-31G(d) method.

TABLE 4. The Population Densities (au) of the p_y-Orbitals of the Carbon and M Atoms in the Molecules of Compounds I, Ia, II, IIa

Molecule	M	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$
I*	1,742	1,025	1,067	1,067	1,025
I*[2]	1,740	1,022	1,068	1,071	1,019
II*	1,637	1,055	1,089	1,088	1,056
Ia*	1,746	1,0505	1,072	1,056	1,031
IIa*	1,6425	1,088	1,086	1,080	1,055

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* RHF/6-31G(d) method.

*[2] RMP 2/6-31G(d) method.

TABLE 5. The Energies (E, eV) of Some MOs in the Molecules of Compounds I, Ia and II, IIa, Calculated by the RHF/6-31G(d) Method, and the Vertical Ionization Potentials (I_B, eV) of Compounds I and II [10]

I			Ia	II		
$-E$	$-E$*	I_B	$-E$	$-E$*	I_B	$-E$
8,66	8,49	8,89	8,81	7,96	8,21	8,80
10,61	10,63	10,25	11,09	9,16	9,20	9,70
14,47	14,53	13,00	12,81	14,08	12,60	12,56
15,22	15,25	14,40	13,59	14,81	13,00	13,12
15,68	15,51	15,25	15,11	15,29	13,70	14,72
16,56	16,41	15,60	15,77	15,69		15,40
20,14	19,92	18,80	16,95	19,95		16,29
21,07	21,13	19,70	18,09	20,76		16,73
22,00	21,74	23,10	19,99	21,44		19,49
27,42	27,11	24,50	21,17	26,51		21,45
29,41	29,32		22,70	28,22		21,92
39,90	39,43		27,04	35,09		26,26

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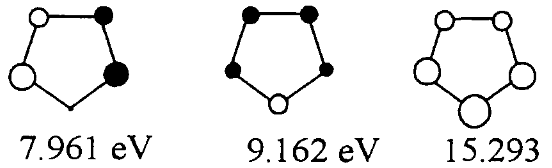
* RMP 2/6-31G(d)//RMP 2/6-31G(d) method.

Some contribution to the decrease in the NQR frequencies of the derivative IIa compared with Ia [see Eq. (1)] is made by the lower half-sum of the population densities of the $3p$-constituents of the valence p_x- and p_y-orbitals of the chlorine atom (by 0.005) in the first compound. This decrease is due to a larger degree to the higher population density of its p_z ($p\sigma$)-orbital in the given molecule (by 0.008). In 2-chlorothiophene the half-sum of the population density of the $3p$-constituents of the valence p-orbitals of the chlorine atom is even lower (1.317) than in Ia (1.320). The higher ^{35}Cl NQR frequency of 2-chlorothiophene compared with that of Ia can therefore be due only to the lower population density of the $3p$-constituents of the valence p_z($p\sigma$)-orbital of its chlorine atom (0.925). The asymmetry parameter of the electric field gradient at the ^{35}Cl nuclei in 2-chlorothiophene, calculated from the population density of the $3p$-constituents of the valence p-orbitals of the chlorine atom [4], is somewhat lower than in Ia but higher than in IIa (Table 2) and does not characterize the degree of its participation in p,π-conjugation [1, 6], as supposed earlier (e.g., see [5]).

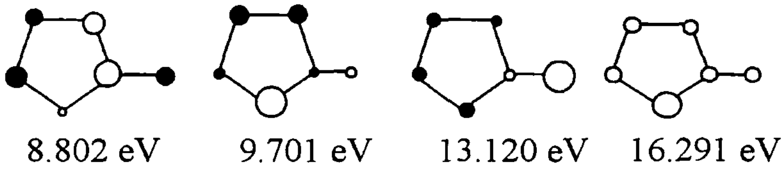
Since the molecules of I, Ia, II, IIa are planar, it is possible to analyze the populations of the p_y-orbitals of their atoms (Cl, C, O, N). As seen from Table 4, the p_y-orbitals of the heteroatoms are electron-deficient, while those of the carbon atoms are electron-sufficient. According to the usual theories, this is due to the conjugation between the unshared electron pairs of the heteroatoms and the corresponding π-electron system.

The configuration of the oxygen atom in the molecules of I and Ia can be considered tetrahedral (the orbitals of the unshared electron pairs are directed toward the apices of the tetrahedron). It is not therefore possible to calculate correctly the degree of delocalization at the carbon atoms of the ring on the basis of the results of the calculations performed. Since the orbital of the unshared electron pair of the nitrogen atom in compounds II and IIa is perpendicular to the plane of the ring, its population density can characterize the degree of its participation in interaction with the π-electron system. In the molecule of II the electron deficiency at the p_y-orbital of the nitrogen atom amounts to 0.363, while the total excess density at the carbon atoms of the pyrrole ring is 0.288. In the derivative IIa the total deficiency of electron density at the p_y-orbitals of the nitrogen and chlorine atoms is 0.358 + 0.038 = 0.39, while the total excess at the carbon atoms of the ring is 0.309. Consequently, the unshared electron pairs of the heteroatoms in the molecules of II and IIa are not localized solely at the π-system of the heterocycle.

The electronic structure of five-membered heterocyclic compounds was studied theoretically and experimentally by photoelectron spectroscopy [9, 10]. The energies of the individual MOs obtained by us for the molecules of I and II (Table 5) differ somewhat from those given in literature. The calculation of system I by the RMP2/6-31G(d) method with regard to electron correlation did not lead to an improvement in the agreement (Table 4). However, these MOs are similar in form. Some of the MOs in compounds II and IIa are shown below as an example.



II



IIa

The highest occupied MOs of the molecules of I, Ia, II, IIa are formed almost completely from the p_y-orbitals of the carbon atoms of the ring, while the p_y-orbital of the M atom makes a substantial contribution to the neighboring occupied MO, which is antibonding, and also to the bonding MO. The composition of the bonding MOs corresponds to concepts concerning p,π-conjugation between the unshared electron pairs of the M atoms and the π-electron system of the five-membered ring. However, the participation of the orbitals of these unshared pairs in the construction of other MOs does not make it possible to assess the contribution from this conjugation to the electron-density distribution, which determines the physical characteristics of the investigated heterocyclic compounds.

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