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ab initio CALCULATIONS OF THE GEOMETRICAL AND ELECTRONIC STRUCTURE OF THIOPHENE AND 2-CHLOROTHIOPHENE MOLECULES

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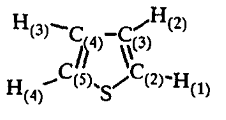
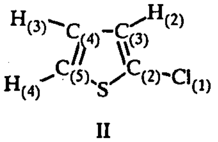
Features of the structure of thiophene and 2-chlorothiophene molecules have been analyzed from the results of ab initio calculations using the RHF/6-31G* method.

The NQR frequencies of the halogen atoms in substituted 2-chloro and 2-bromothiophenes are significantly higher than in the corresponding halobenzene analogs despite the fact that the electronegativities of the S and C(sp^2) atoms are virtually identical. This is usually explained by conjugative effects (see, for example, [1, 2]). Analysis of the experimental data for a considerable number of compounds containing the Y—C—M or Y—C=M groups (Y is an indicator atom), among which are substituted 2-halothiophenes, has led to the conclusion that the mechanism of the noninductive effect of the atom M on Y is basically the same for any M and Y: polarization of the C—Y bond through the influence of the charge of atom M is directly via the field (see, for example, [2, 3]).

For further study of the features of interaction of the atoms in the groups Y—C—M and Y—C=M, particularly for thiophene and its derivatives, and to define the reasons for the abnormally high NQR frequencies in 2-halothiophenes, we have carried out *ab initio* calculations for thiophene (I) and 2-chlorothiophene (II) by the restricted Hartree-Fock method resolved on the 6-31G* basis and with full optimization of their geometries. Calculations were performed using the Gaussian 92 program [4]. As the initial point of the coordinate system H_1 or Cl atoms were chosen. The axis Z coincided with the $H_{(1)}$—$C_{(2)}$ or Cl—$C_{(2)}$ bonds and the Y axis was perpendicular to the plane of the molecule. In the basis used, each atomic valence *p*-orbital represented a combination of two orbitals of different types (2*p* and 3*p* for the C atoms and 3*p* and 4*p* for the S and Cl atoms).



I



II

According to the results of the optimization of the geometry, both molecules are planar. In them, all dihedral angles are 0 or 180°±0.03°. The lengths of the corresponding bonds in both molecules are virtually equal with an insignificant difference in the angles between the bonds (Table 1).

$$\nu = (e^2Qq_{\text{ат}}/2h)[(\mathrm{N}p_x + \mathrm{N}p_y)/2 - \mathrm{N}p_z](1 + \eta^{2/3})^{1/2} \qquad (1)$$

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TABLE 1. Bond Lengths (d) and Angles Between Them (α) in Molecules of Thiophene I and 2-Chlorothiophene II

Bond	*d*, Å		Angle	α, deg	
	I	II		I	II
C—S	1,726	1,729	$C_{(2)}$—S—$C_{(5)}$	91,3	90,5
$C_{(2)}$—$C_{(3)}$	1,345	1,344	S—$C_{(2)}$—$C_{(3)}$	111,8	112,1
$C_{(3)}$—$C_{(4)}$	1,437	1,437	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	112,5	112,9
$C_{(2)}$—H	1,071	-	$H_{(1)}$—$C_{(2)}$—S	120,4	-
$C_{(2)}$—Cl	-	1,721	Cl—$C_{(2)}$—S	-	120,6

We have previously shown that the ^{35}Cl (ν) NQR frequencies for the chlorine-containing molecules and also the asymmetry parameters of the electric field gradient on the ^{35}Cl nuclei in them, as calculated by equation (1), and the populations for the 3*p*-components of the Cl atom valence *p*-orbitals (as found using the RHF/6-31G* method) are in agreement with experimental values [2, 5-7]. This allows one to use the experimental ^{35}Cl NQR data to check the correctness of the quantum-chemical calculations of the distribution of electron density in the molecules. The features of these distributions, in their turn, allow one to judge on the nature of interaction of AO's in the molecules. The ^{35}Cl NQR frequency in molecule II, calculated by this method (ν = 36.477 MHz) is close to the experimental value (ν^{77}_{mean} = 36.961 MHz [1]), showing the correctness of the calculated populations for the Cl atom valence *p*-orbitals in molecule II. The latter then gives insight into the reason for the anomalously high ^{35}Cl NQR frequencies for 2-chlorothiophenes and its substituted products when compared to the corresponding chlorobenzene derivatives.

Unfortunately, the asymmetry parameter for the gradient of electric field for the ^{35}Cl nuclei in 2-chlorothiophene was not measured. However, it can be reckoned from the populations of the 3*p*-components of the Cl atom valence *p*-orbitals. It proves to be significantly less (η = 2.49 %) than in the majority of substituted chlorobenzenes [10].

Table 2 shows the Cl atom valence *p*-orbital populations calculated by the RHF/6-31G* method for the Cl atom in molecule II and their 3*p*- and 4*p*-components, together with the C and S atom p_y-orbitals in compounds I and II. For comparison, the analogous populations for the C and Cl atoms in chlorobenzene [6] are included. The populations of the 3*p*-components of the p_x- and p_y- orbitals of the Cl atom in II are somewhat higher than in chlorobenzene. According to equation (1), this introduces some contribution to the increase in the ^{35}Cl NQR frequency for 2-chlorothiophene when compared to chlorobenzene. The average indicated populations $(\mathrm{N}p_x+\mathrm{N}p_y)/2$ have values of 1,317 and 1.310 respectively. However, a significantly greater contribution to this

TABLE 2. Populations of the Valence *p*-Orbitals of the Cl Atom in Molecule of II and Chlorobenzene III, the p_y-Orbitals in Molecules of I-III (ΣN*p*) and their Components (2*p*, 3*p*, and 4*p*).

Mole-cule	Orbi-tal	Cl			N*py*				
		N*px*	N*py*	N*pz*	S	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$
I	2*p*					0,562	0,544	0,543	0,563
	3*p*				1,146	0,519	0,471	0,471	0,520
	4*p*				0,595	-	-	-	-
	ΣN*p*				1,741	1,081	1,015	1,014	1,083
II	2*p*					0,613	0,552	0,544	0,566
	3*p*	1,320	1,314	0,925	1,163	0,511	0,457	0,466	0,517
	4*p*	0,640	0,642	0,172	0,581	-	-	-	-
	ΣN*p*	1,960	1,956	1,097	1,744	1,124	1,009	1,010	1,083
III	2*p*					0,574	0,532	0,514	0,522
[6]	3*p*	1,316	1,303	0,946		0,465	0,462	0,462	0,471
	4*p*	0,650	0,656	0,191		-	-	-	-
	ΣN*p*	1,966	1,959	1,137		1,039	0,994	0,976	0,993

increase relates to the much smaller population of the 3*p*-components for the Cl atom p_z-orbitals in II compared to chlorobenzene. This agrees with the explanation of the observed experimental NQR frequency ratios for substituted 2-halothiophenes and halobenzenes through polarization of the C—halogen bond via the action of the geminal S or C(sp^2) atom. Such a mechanism is also supported by the charges on the atoms in these molecules as calculated by the RHF/6-31G* method (Table 3). The significant positive charge on the S atom in thiophene and its 2-chloro derivative polarizes the $C_{(2)}$—$C_{(3)}$, $C_{(4)}$—$C_{(5)}$, $C_{(2)}$—$H_{(1)}$, and $C_{(2)}$—Cl bonds geminal to it directly via the field. In this way there arises a quite large negative charge on the neighboring carbon atoms (on the geminal carbons a smaller negative charge, on the Cl atom in compound II a slight positive charge, and on atoms $H_{(1)}$ and $H_{(4)}$ the greatest positive charge (Table 3)).

The overall populations (N_{3p} + N_{4p}) of the valence p_x- and p_y-orbitals of the Cl atoms in molecules of II and chlorobenzene are almost identical. There is only a difference in the overall population of the p_z-orbitals (Table 2) which points to an almost identical type of interaction of the Cl atom with other atoms in the two investigated molecules.

All of the C atoms in chlorobenzene, with the exception of that bound with the Cl atom, have some π–electron deficit. In molecules of I and II, all of the C atoms are electron excessive (Table 2), moreover the greatest excess is characteristic of the C atoms directly bonded to the sulfur atom. This corresponds with polarization of the C—C π–bonds geminal in relation to the latter, under the action of the significant positive charge of the S atom directly through the field. In pyridine and its 2- and 3-chloro-substituted derivative, a similar polarization of the geminal C—C π–bonds, but in a opposite sense, is due to the effect of the negative charge on the N atom [7].

Bearing in mind the small excess of π–electron density on all of the C atoms of molecules I and II, which is absent in chlorobenzene, it can be assumed that the reason for it is participation of the p_y-orbital of the S atom in *p*,π–conjugation with the π–electrons of the thiophene ring C atoms. This agrees with the inclusion in the make up of the binding MO in molecules of I (-14.1 eV) and II (-15.2 eV) of the p_y-orbitals of all the C atoms and also the S and Cl atoms (in molecule II). At the same time, these AO participate in formation of a series of other MO and so it is evidently not necessary to account for the small excess of the π–electron density on the C atoms of the thiophene ring by *p*,π–conjugation.

In molecules of I and II, the *d*-orbitals of the S atom are slightly populated but much the same as the *d*-orbitals of the C atoms. As an example, in Table 4 the populations of the *d*-orbitals of the S and $C_{(3)}$ atoms are given and this permits their comparison. Correlation of the data in Table 4 confirms the conclusion (see, for example [8, 9]) regarding the insignificant contribution of the *d*-orbitals of the S atom into the chemical bonding of thiophene.

TABLE 3. Charges on the Atoms in Molecules of I and II Calculated by the RHF/6-31G* Method.

Molecule	$H_{(1)}$, Cl	S	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$
I	0,232	0,285	-0,411	-0,171	-0,171	-0,411	0,208	0,208	0,232
II	0,035	0,346	-0,337	-0,153	-0,163	-0,420	0,230	0,219	0,241

TABLE 4. *d*-Orbital Populations for the S and $C_{(3)}$ Atoms in Molecule of I

Atom	d_{xx}	d_{yy}	d_{zz}	d_{xy}	d_{xz}	d_{yz}
S	0,232	0,285	-0,411	-0,171	-0,171	-0,411
$C_{(3)}$	0,035	0,346	-0,337	-0,153	-0,163	-0,420

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