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CONDENSED HETEROCYCLES. 39.* QUANTUM-CHEMICAL CALCULATIONS OF THE REACTIVITIES OF SOME CONDENSED SULFUR AND SELENIUM HETEROCYCLES

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A number of isomeric thienothiophenes, selenophenothiophenes, and selenophenoselenophenes, as well as their C-protonated forms (σ complexes), were calculated by the self-consistent-field (SCF) MO LCAO method with the CNDO/2 approximation and the spd basis. Their reactivities in electrophilic substitution reactions were investigated theoretically by means of the localization energy approach. The results were compared with the available experimental data. The dependence of the specificity of electrophilic attack on the size of the attacking reagent was investigated for compounds with various heteroatoms. It is shown that the reactivity of the α position relative to the selenium atom should increase as the size of the attacking reagent increases.

The specific characteristics of the chemical behavior of a heteroaromatic compound are known to be due to the presence in the molecule of a heteroatom, which is not only a "supplier" of electrons for the formation of an aromatic π-electron structure but also an orienter that determines the specificity of attack by electrophilic or nucleophilic agents. The picture is complicated when one examines condensed systems. In this case not only the type of condensation (the mutual orientation of the heteroatoms) but also the electronic effects due to the nature of the heteroatoms have a considerable effect on the physical properties and reactivities of the compounds. Condensed heteroaromatic systems, particularly those that include different heterocycles, are therefore interesting subjects for the study of the effect

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*See [1] for communication 38.

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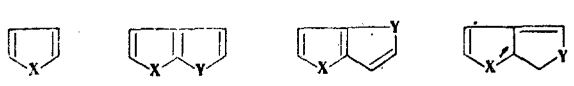
of the type of condensation and the nature of the heteroatom on their reactivities [2, 3].



I, II III–V VI–VIII IX–XII

Scheme 1

I X=S; II X=Se; III X, Y=S; IV X=S, Y=Se; V X, Y=Se; VI X, Y=S; VII X=S, Y=Se; VIII X, Y=Se; IX X, Y=S; X X=Se, Y=S; XI X=S, Y=Se; XII X, Y=Se

In the present research we made calculations of thiophene, selenophene, and various isomeric thienothiophenes, selenothiophenes, and selenophenoselenophenes (Scheme 1), as well as all of the possible C-protonated forms (σ complexes), by the self-consistent-field (SCF) MO LCAO method within the CNDO/2 valence approximation [4]. The calculations were made within the spd basis for the sulfur and selenium atoms [5] with the aid of the parameters of Hase and Schweig [6]. The experimental geometries of the thiophene and selenophene rings [7, 8], with r_{CH} = 1.08 Å, were used in the calculations. It was assumed that in the case of condensation the lengths of all of the C—C bonds except the central bond remain the same as in the starting heterocycles; the lengths of the central bonds were optimized (their values are presented in Table 1). The so-called standard geometry (e.g., see [9]) was assumed for the σ complexes, i.e., the geometry of the ring remains unchanged in the case of protonation, whereas the geminal node (the site of addition of the proton) has the geometrical parameters r_{CH} = 1.08 Å and $\angle$H—C—H = 109°28', and the projections of the CH bonds on the plane of the ring coincide with the direction of the CH bond in the starting heterocycle.

We examined the reactivities of the heterocycles indicated above in electrophilic substitution reactions. The charges on the carbon atoms (Q_C) (static index) and the localization energy (Λ^+) (dynamic index) were used as reactivity indexes. Within the CNDO/2 approximation (or any other valence or all-electron approach), Λ^+ is defined as:

$$\Lambda^+ = E_{tot}{}^{M} - E_{tot}{}^{MH+}, \tag{1}$$

where E_{tot}^{M} and E_{tot}^{MH+} are the total energies of the aromatic molecule and its σ complex with a proton, respectively. The calculated Q_C and $\Delta\Lambda^+$ values (relative to the 3 position in thiophene) are presented in Table 1. As we have already noted in [10] for thienothiophenes, the Q_C values give only qualitative agreement (within the limits of a single molecule) with the experimental data on electrophilic substitution. However, when it is necessary to compare the reactivities of different positions of different molecules on a semiquantitative level,

TABLE 1. Calculated $\Delta\Lambda^+$ and Q_C Values for Thiophene (I), Selenophene (II), Thienothiophenes (III, VI, and IX), Selenophenothiophenes (IV, VII, and XI), and Selenophenoselenophenes (V, VIII, and XII)

Compound	Length of the central bond, Å	Position	$\Delta\Lambda^+$, kcal/mole	Q_C, e
I		2	17,9	−0,037
		3	0,0	0,030
II		2	17,3	−0,043
		3	1,7	0,040
III	1,40	2	24,2	−0,031
		3	9,0	0,021
IV	1,40	2	25,7	−0,034
		3	10,7	0,027
		4	8,3	0,036
		5	21,9	−0,043
V	1,38	2	22,7	−0,034
		3	9,5	0,021
VI	1,38	2	31,2	−0,041
		3	5,1	0,055
VII	1,39	2	31,6	−0,041
		3	6,5	0,053
		5	28,6	−0,045
		6	4,3	0,062
VIII	1,38	2	28,1	−0,046
		3	5,1	0,061
IX	1,44	2	23,3	−0,022
		3	10,0	0,026
		4	44,1	−0,063
		6	35,1	−0,019
X	1,44	2	20,5	−0,029
		3	8,7	0,034
		4	44,5	−0,065
		6	36,9	−0,012
XI	1,44	2	25,5	−0,020
		3	11,1	0,022
		4	41,3	−0,072
		6	32,6	−0,022
XII	1,44	2	22,5	−0,028
		3	9,3	0,030
		4	42,0	−0,072
		6	34,6	−0,015

one must use the Λ^+ values. The relationship between the experimental rate constants and the values calculated from the expression,

$$\lg k_i/k_0 = C\Delta\Lambda^+ \tag{2}$$

for the reactions of thiophene and isomeric thienothiophenes with various electrophiles is presented in Fig. 1 as an example. In Eq. (2), k_i is the rate constant for substitution in the investigated position, k_0 is the rate constant for substitution in the 3 position of thiophene, and $\Delta\Lambda^+$ is the difference in the localization energies in the indicated positions; the C coefficient was determined by the method of least squares. Unfortunately, quantitative experimental data of this type are not available for isomeric selenophenothiophenes and selenophenoselenophenes, although there have been comparative qualitative studies of the relative activities of various positions in these compounds for some of them, particularly selenopheno[2,3-b]thiophene (IV) and selenopheno[3,2-b]thiophene (VII), in formylation and bromination reactions [1, 3] that provide evidence for the greater activity of the α positions relative to selenium as compared with the α positions relative to sulfur. This is not in agreement with the localization energies calculated in the present research. The reason for this disagreement evidently should be sought in the possible dependence of the specificity of electrophilic attack on the size of the attacking reagent. The importance of this effect in heteroaromatic systems, which is manifested in the form of a direct stabilizing interaction between the heteroatom and the attacking electrophile during the formation of the σ complex, was first pointed out in [12].

The effect of the size of the attacking electrophile on the specificity of electrophilic substitution in IV and VII was investigated in the present research with the aid of the CNDO/2 method supplemented by the possibility of the introduction of "pseudoatoms" in the calculation. The concept of "pseudoatoms" within the framework of the CNDO/BW method was initially formulated for the description of adsorption and heterogeneous catalysis processes on the basis of a cluster model [13]. The idea of this approach consists in replacement of any group of atoms or even part of the solid by some one-orbital "pseudoatom" with specifically selected quantum-chemical parameters. In our case the "pseudoatom" (a one-orbital atom with an 1s AO and an effective charge on the nucleus of unity) models the electrophile, which, as is well known, may be either monoatomic or consist of several atoms. It is clear that in the case of a sufficiently large electrophile the "pseudoatom" will model only its reaction center, whereas the effect of the remaining atoms on the latter will be taken into account by the parameters of the "pseudoatom." In our case we selected the Slater exponents ξ, a change in which made it possible to model the change in the size of the electron cloud of the electrophile and the change in its coulombic interaction with the heteroring, as the variable parameters. The remaining calculated parameters of the "pseudoatom" were assumed to be equal to the parameters of the hydrogen atom in the CNDO/2 method.

The following values of the variable exponent of the AO of the "pseudoatom" were used in the calculations: 1.2 (the standard value of the CNDO/2 method for the hydrogen atom), 1.0, 0.8, and 0.6. These values virtually correspond to an increase in the

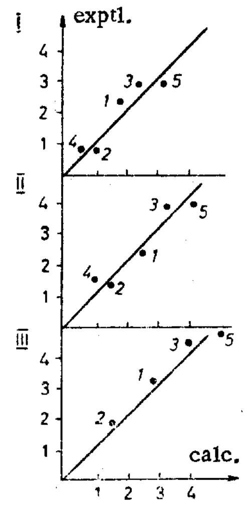


Fig. 1. Relationship between the calculated and experimental rate constants for the acetylation (I), chlorination (II), and formylation (III) of thiophene and isomeric thienothiophenes relative to the 3 position in thiophene: 1) thiophene (I) (2-position); 2) thieno[2,3-b]thiophene (III) (3 position); 3) thieno[2,3-b]thiophene (III) (2 position); 4) thieno[3,2-b]thiophene (VI) (3 position); 5) thieno[3,2-b]thiophene (VI) (2 position).

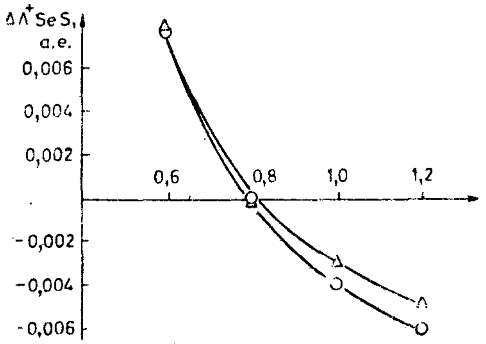


Fig. 2. Dependence of $\Delta\Lambda_{SeS^+}$ on the Slater exponent ξ of the "pseudoatom" of the electrophile: ○) selenopheno[2,3-b]thiophene (IV); Δ) selenopheno[3,2-b]thiophene (VII).

size of the "pseudoatom" of the electrophile in the indicated order. The dependences of the $\Delta\Lambda_{SeS^+}$ values (the differences in the localization energies with respect to the α positions relative to sulfur and relative to selenium) on the ξ value of the "pseudoatom" are presented in Fig. 2.

As a result of a decrease in ξ (i.e., an increase in the size of the attacking reagent), electrophilic attack at the α position relative to selenium becomes more preferred in both IV and VII when ξ = 0.8, and the yield of the product of this substitution should increase as ξ decreases. This is in agreement with the observed experimental fact [1, 3] that the yield of the product of substitution at the α position relative to selenium reaches 55-65% in the case of formylation in the systems under consideration, whereas the yield reaches 87-100% in the case of bromination.

Thus the use of the method of reactivity indexes supplemented by the "pseudoatom" approach makes it possible to sufficiently accurately interpret the experimental data on electrophilic substitution in condensed heteroaromatic systems with various heteroatoms.

In conclusion, let us note that the effect of the dependence of the specificity of electrophilic attack on the nature (particularly the size) of the attacking electrophile will also basically determine the difference in the reactivities of condensed heterocycles with various heteroatoms, since their remaining characteristics (localization energies and charges on the atoms) do not change very substantially in the case of successive replacement of one or two sulfur atoms by selenium in the thienothiophene molecule, as one can see from Table 1.

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