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MODERN QUANTUM-CHEMICAL STUDY OF THE ELECTRONIC STRUCTURE AND REACTIVITY OF THIOPHENE

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Abstract

Thiophene is a unique sulfur-containing heterocyclic compound with one sulfur atom. It is a colorless liquid with the formula C_4H_4S , boiling point 84.1 °C, and a benzene-like odor. It is poorly soluble in water but readily soluble in organic solvents. Thiophene continues to fascinate organic chemists with its wide range of chemical properties, ultimately inspiring both theoreticians and experimentalists to conduct fundamental scientific research and conduct new reactions to create innovative organic compounds with high yields. Numerous biologically active drugs are obtained from it, and they are widely used, particularly in agriculture, medicine, and pharmaceuticals. In halogenation, nitration, and formylation reactions, α -substituted products are obtained more rapidly and are exclusively the main products relative to others. Therefore, it is of theoretical interest to identify the key factors behind thiophene's unique behavior by studying its geometric parameters and electronic structure. This article presents the results of quantum chemical calculations performed by us using the Gaussian program to calculate the geometry and electronic structure, and to evaluate the reactivity of thiophene with respect to electrophilic reagents.

Keywords: thiophene, aromatic compound, quantum chemical calculation, Gaussian program, B3LYP method, electronic structure, reactivity, geometry, total energy, frontier molecular orbital, correlation, product ratio

Introduction

Depending on its π -excess, thiophene is significantly more active than benzene in electrophilic substitution reactions, sometimes up

to 100,000 times more so. Under normal conditions, reactions are known to proceed exclusively to the α -position, 2–3 orders of magnitude faster than to the β -position of the ring

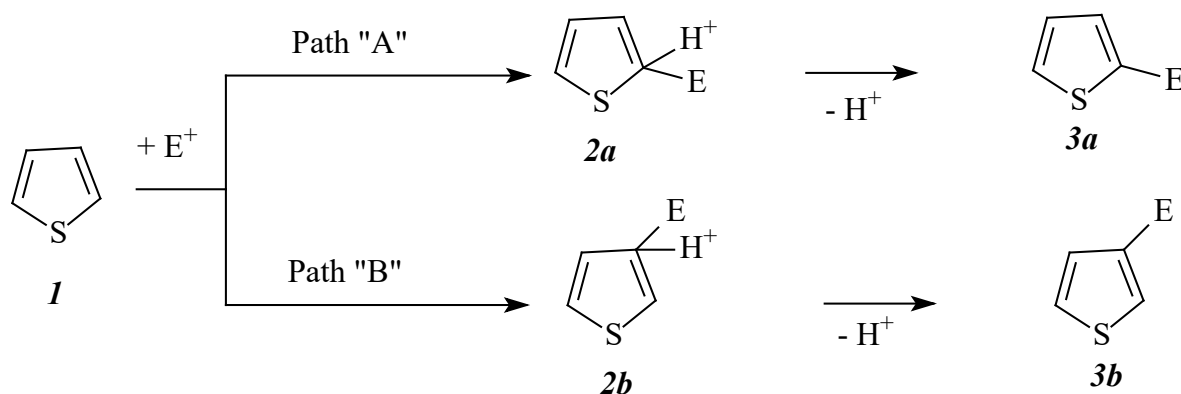
(Spivey Alan C., 2012; Molina P., Arques A., Cartagena I., 2008; Yurovskaya M. A., Kurkin A. V., Lukashev N. V., 2007). This behavior inspired us to conduct theoretical quantum chemical calculations to establish the precise geometry and electronic structure of thiophene. Based on calculations performed in the Gaussian program (Frisch M. J., Trucks G. W., et al., 1998) using the B3LYP method, we estimated the potential reactivity of the α - and β -positions of the heterocycle and established a correlation between the theoretical data and the productivity of the reactions. In the world literature there are numerous experimental (Fahimeh Abedinifar, Elham Babazadeh Rezaei. et al., 2021; Amita Vyasa, Dharmesh Katariya, et.al., 2025). and theoretical results of syntheses carried out with the participa-

tion of thiophene and their derivatives for the analysis of data according to the MO theory (Michael Dewar, Ralph C. Dougherty. 1975; Dipak Kumar Mandal. 2025). In this article, an analysis of the results of theoretical calculations by quantum chemistry methods is carried out to determine the exact geometry, electronic structure, reactivity of thiophene and to establish a correlation between the experimental ratios of the yield of the α -/ β -substitution reaction of reagents.

Research Objects

We chose thiophene, an aromatic five-membered heterocycle with one sulfur atom, and its transformation products in electrophilic substitution reactions as our research object.

Figure 1. Scheme of the electrophilic substitution reaction of thiophene



Methods and Results

We used the DFT-B3LYP method with the 3–21G basis set for quantum chemical studies of thiophene and its monosubstituted derivatives in our calculations. In previous articles, we successfully used the Gaussian98 software package (Mamarakhmonov M. Kh., Belen'kii L. I. et. al., 2016) for the calculation of several heteroaromatic compounds. During the calculations, all geometric pa-

rameters of thiophene, its intermediates, and derivatives (Fig. 1) were fully optimized.

We performed theoretical calculations and obtained reliable data, which are now being analyzed quantitatively. This approach to solving the problem of determining the precise electronic structure and assessing reactivity yielded the desired results, which serve as an addition to the knowledge base on heterocycles.

Table 1. Total energy, geometry of objects and net atomic charges

Energy (Et, ΔE), dipole moment (μ) of compounds					
	1	2a	2b	3a	3b
Et	–345246.03	–369993.12	–369978.37	–369785.98	–369784.73
ΔE		0*	14.75	0*	1.25
μ , D	0.97	1.95	1.17	1.06	1.36

Energy (Et, ΔE), dipole moment (μ) of compounds					
	1	2a	2b	3a	3b
Bonds	Bond length, (d, Å)**				
S1-C2	1.808	1.926	1.702	1.823	1.808
C2-C3	1.358	1.484	1.474	1.360	1.360
C3-C4	1.442	1.368	1.502	1.442	1.449
C4-C5	1.358	1.414	1.335	1.357	1.356
C5-S1	1.808	1.728	1.860	1.809	1.807
C2-C6		1.553		1.498	
C3-C6	1.081		1.595		1.512
Atoms	Atomic charges, (q, e)**				
S1	0,515	0.758	0.849	0.512	0.511
C2	−0,539	−0.599	−0.444	−0.336	−0.557
C3	−0,146	−0.047	−0.392	−0.147	0.073
C4	−0,146	−0.124	−0.042	−0.146	−0.139
C5	−0,539	−0.517	−0.501	−0.54	−0.540
C6		−0.546	−0.528	−0.602	−0.606

* – Here the value of the total energy of these compounds is taken as the starting point

** – For precise analysis, data is presented in thousandths

Table 1 below presents the results of calculations of the geometry and electronic structure of the substrate (**1**), model intermediates (**2a**, **2b**), and the products of electrophilic substitution of thiophene (**3a**, **3b**), which provide a quantitative picture of the methylation process.

Discussion of the results

According to Table 1, the total energy of the starting substrate **1** is $E_t = -345246.03$ kCal/mol, the dipole moment is $\mu = 0.97$ D and the dipole vector is directed from the heteroatom to the middle of the C3-C4 bond (Fig. 2). The symmetrical, planar arrangement of the ring atoms relative to the heteroatom and the presence of 6π electrons in the ring (preservation of the Hückel rule) makes the molecule aromatic. At the same time, the symmetry in the bond lengths and the values of the valence and torsion angles is preserved. The energetic preference of compound **2a** relative to **2b** by $\Delta E_t = -14.75$ kCal/mol.

The electron charges at the α - and β -positions of thiophene are different: $q = -0.539e$ and $q = -0.146e$, respectively, indicating the advantage in nucleophilic reactivity of the α -position relative to the β -position. To more

accurately study the electrophilic substitution process and reaction mechanism, we also calculated the geometry and electronic structure of charged structures **2a** and **2b**, representing the process intermediates (Fig. 1).

Geometry of compounds

After the substitution of the methyl cation CH_3^+ in the α -position of the substrate, i.e. in the process **1**→**2a** (Path “A”, Fig.1), a redistribution of electron charges occurs and the lengths of the S1-C2, C2-C3, C4-C5 bonds are lengthened by $\Delta d = 0.118\text{\AA}$, $0.126\text{\AA}$, $0.056\text{\AA}$, and the C3-C4, C5-S1 bonds are shortened by $\Delta d = 0.074\text{\AA}$, $0.080\text{\AA}$. For example, the C2 atom (α -position) of isomers **2a** and **2b** is concentrated with the maximum negative charge equal to $q = -0.599e$ and $q = -0.444e$, respectively, whereas the C5 atom, located symmetrically to the first, carries a charge of $q = -0.517e$ and $q = -0.501e$, respectively.

Conclusions

The α -positions of thiophene exhibit greater reactivity relative to the β -positions of the substrate, both in charge-controlled reactions and in orbital control. The difference $\Delta E_t = 1.25$ kCal/mol in the total energies

of products **3a** and **3b** once again shows the preference of the reaction path **1**→**2a**→**3a** (reaction pathway 1, see Fig.1).

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Dedicated

to the memory of Doctor of Chemical Sciences, Professor Leonid I. Belenkii

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