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FREE ENERGIES OF 2-AMINO-1,5-DIAZASPIRO[4.5]DEC-1-EN-5-IUM CHLORIDES MONOHYDRATES AND ARYLSULFONATES FORMATION AT β-AMINOPROPIOAMIDOXIMES ARYLSULFOCHLORINATION

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Abstract: *Introduction.* We have previously obtained new spiropyrazolinium compounds by arylsulfochlorination of β-aminopropioamidoximes. But it was found that under certain conditions, the main or by-product of β-(thiomorpholine-1-yl)propioamidoxime tosylation was 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate. In the case of other β-aminopropioamidoximes, only 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium arylsulfonates were isolated. *The aim of the work* is to perform a theoretical comparison of reactions of tosylation, *para*- and *ortho*-nitrobenzenesulfochlorination of β-aminopropioamidoximes and evaluate the propability of 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium chlorides monohydrates formation. *Methodology.* The calculations were performed using Gaussian 09 package by DFT/B3LYP/6-31G++(d,p) method. *Results and discussion.* Thermodynamically preferred products were identified by comparing the Gibbs free energies of reactions. Chemical stability and reactivity parameters for 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate, tosylate, *para*-nitrophenylsulphonate and *ortho*-nitrophenylsulphonate were predicted based on calculated HOMO and LUMO energies. In most cases arylsulfonates are thermodynamically favorable, except when the initial substrate is β-(thiomorpholine-1-yl)propioamidoxime. *Conclusion.* 2-Amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate is more preferred compared to the corresponding arylsulphonates.

Key words: β-aminopropioamidoximes, arylsulfochlorination, DFT method, HOMO–LUMO analysis, Gaussian 09

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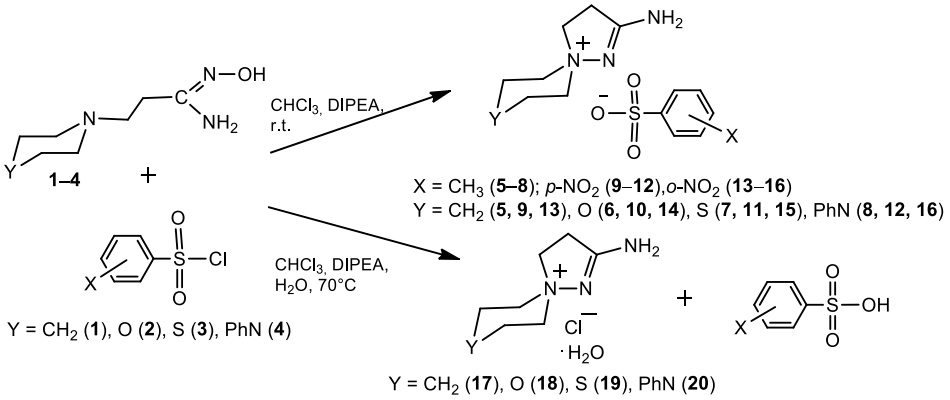
1. Introduction

As we previously reported [1–3], tosylation and para-nitrobenzenesulfonchlorination of β-aminopropionamidoximes **1–4** (β-amino groups were: piperidin-1-yl-, morpholine-1-yl-, thiomorpholine-1-yl- and 4-phenylpiperazin-1-yl) leads to the formation of the corresponding 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium arylsulfonates, and in the case of β-(benzimidazole-1-yl)propioamidoxime products are O-arylsulfo derivatives.

When optimizing the conditions for β-aminopropioamidoximes arylsulfochlorination, it was found that under certain conditions (when heating the reaction mixture in chloroform in the presence of N,N-diisopropylethylamine DIPEA), the main or by-product of β-(thiomorpholine-1-yl)propioamidoxime tosylation was 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate **19**. The experiment did not provide for carrying out β-aminopropioamidoximes arylsulfochlorination reactions in an inert medium. The high hygroscopicity of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride determines its existence as a monohydrate.

In the case of other β-aminopropioamidoximes (**1**, **2** and **4**) arylsulfochlorination, only 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium arylsulfonates were isolated. Conditions of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate obtaining, its physical and chemical characteristics, NMR ^{1}H and ^{13}C spectra and X-ray diffraction data were given in [4].

This paper presents the results of a theoretical comparative study of reactions and propability of 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium chlorides monohydrates **17–20** formation in the reactions of tosylation, *para*- and *ortho*-nitrobenzenesulfochlorination of β-aminopropioamidoximes **1–4**.



Scheme 1 – The reactions of tosylation, *para*- and *ortho*-nitrobenzenesulfochlorination of β-aminopropioamidoximes.

Complete optimization of the molecular geometry and calculations of thermodynamic parameters were performed using Gaussian-09 software [5]. The reliability of DFT/B3LYP method in the calculations of thermodynamic parameters and HOMO-LUMO energies related to the heterocyclic compounds

has been confirmed by previous studies [6–8]. The applied basis 6-31G++(d,p) shows sufficient accuracy in calculating the thermodynamic parameters of organic reactions [9]. Vibrational frequency analysis confirms that the ground states were found (no imaginary frequency). Ionization potential (IP), electrophilic index (ω), electronegativity (χ), chemical softness (σ) and hardness (η) were calculated using HOMO and LUMO energies as reported in literature [10–12].

Solvation effects were accounted for by using the polarizable continuum model (IEFPCM) for chloroform. Thermodynamic functions were determined for standard conditions (1 atm. and 298.15 K).

2. Results and discussion

Thermodynamically preferred products were identified by comparing the Gibbs free energies of the corresponding chemical reactions calculated by the Hess equation as the difference between the free energies of the formation of reaction products and reagents. The calculation results are shown in Table 1.

Table 1 – ΔG values of products **5–16** and **17–20** formation reactions

Product	ΔG_S*, kJ/mol	Product	ΔG_{Cl}**, kJ/mol	ΔG_{Cl} - ΔG_S, kJ/mol
tosylation				
5	-144.29	**17**	-142.14	2.15
6	-129.96	**18**	-130.79	-0.83
7	**-117.26**	**19**	**-125.36**	**-8.1**
8	-119.99	**20**	-129.47	-9.48
para-nitrobenzenesulfochlorination				
9	-163.57	**17**	-151.56	12.01
10	-160.02	**18**	-140.21	19.81
11	**-139.70**	**19**	**-145.88**	**-6.18**
12	-147.61	**20**	-138.89	8.72
ortho-nitrobenzenesulfochlorination				
13	-206.59	**17**	-162.66	43.93
14	-157.56	**18**	-151.31	6.25
15	**-142.80**	**19**	**-145.88**	**-3.08**
16	-154.66	**20**	-149.99	4.67
ΔG_S* – the free energy of formation reactions sulfonates (**5–16**) ΔG_{Cl}** – free energy for the formation of the monohydrates of chlorides (**17–20**)				

Calculations show that in most examples aryl sulfonates are thermodynamically favorable, except cases when the initial substrate is β-(thiomorpholine-1-yl)propioamidoxime **3**. 2-Amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate **19**, based on comparing the values of ΔG reactions, is more advantageous compared to 2-amino-8-thia-1,5-

diazaspiro[4.5]dec-1-en-5-ium tosylate, *para*-nitrophenylsulphonate and *ortho*-nitrophenylsulphonate (**7, 11** and **15**, respectively).

Thermodynamic calculations of the reactions of formation of product **18** compared to **6**, and product **20** compared to **8** are exceptions**.** For the first one, the advantage in free energy is rather insignificant (-0.83 kJ/mol), and for the second one, a difference of -9.48 kJ/mol is observed. However, under the conditions described in [1–3], the formation of chloride monohydrate salts was observed only for the 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium cation **19**.

The formation of monohydrate chloride **17** should be considered the least likely, since the energetic advantage of the formation *of ortho*-nitrophenylsulfonate in β-(piperidine-1-yl)propioamidoxime *ortho*-nitrobenzenesulfochlorination reaction is the largest among the obtained free energy differences in β-aminopropioamidoximes arylsulfochlorination reactions.

For obtained 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate **19** the molecular orbitals were simulated and frontier molecular orbitals (FMO) analysis was performed in comparison with tosylate, *para*-nitrophenylsulphonate and *ortho*-nitrophenylsulphonate of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium (**7**, **11** and **15**, respectively).

FMO analysis is very important to predict chemical stability and reactivity parameters based on HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies. The HOMO energy in absolute value corresponds to the ionization of the orbitals and determines the electron-donor properties and, accordingly, the ability to interact with electrophilic reagents. The LUMO energy determines the electron affinity, i.e. electron accepting properties, their ability to interact with nucleophilic reagents. The reactivity parameters of products **7**, **11**, **15** and **19** reflecting their chemical properties are estimated. Results are presented in Table 2.

Table 2 – Reactivity parameters of products **7**, **11**, **15** and **19**

Reactivity parameters	**7**	**11**	**15**	**19**
HOMO energy (eV)	-6.60	-6.74	-6.72	-6.47
LUMO energy (eV)	-0.62	-3.02	-2.57	-0.61
Energy gap ΔE(LUMO-HOMO) (eV)	5.98	3.72	4.15	5.86
Ionization potential $IP = -E$(HOMO)(eV)	6.60	6.74	6.72	6.47
Electron affinity $EA = -E$(LUMO) (eV)	0.62	3.02	2.57	0.61
Electronegativity $\chi\ (eV) = (I + A)/2$ (eV)	3.61	4.88	4.65	3.54
Hardness $\eta = (IP - EA)/2$ (eV)	2.99	1.86	2.08	2.93
Chemical potential $\mu = -\chi$ (eV)	-3.61	-4.88	-4.65	-3.54
Electrophilicity $\omega = \mu^2/2\,\eta$ (eV)	2.18	6.40	5.20	2.14
Softness $\sigma = 1/\eta$ (eV)	0.33	0.54	0.48	0.34

Figure 1 shows 3D plots of HOMO and LUMO. GaussView 05 program [13] was used to visualize molecular orbitals.

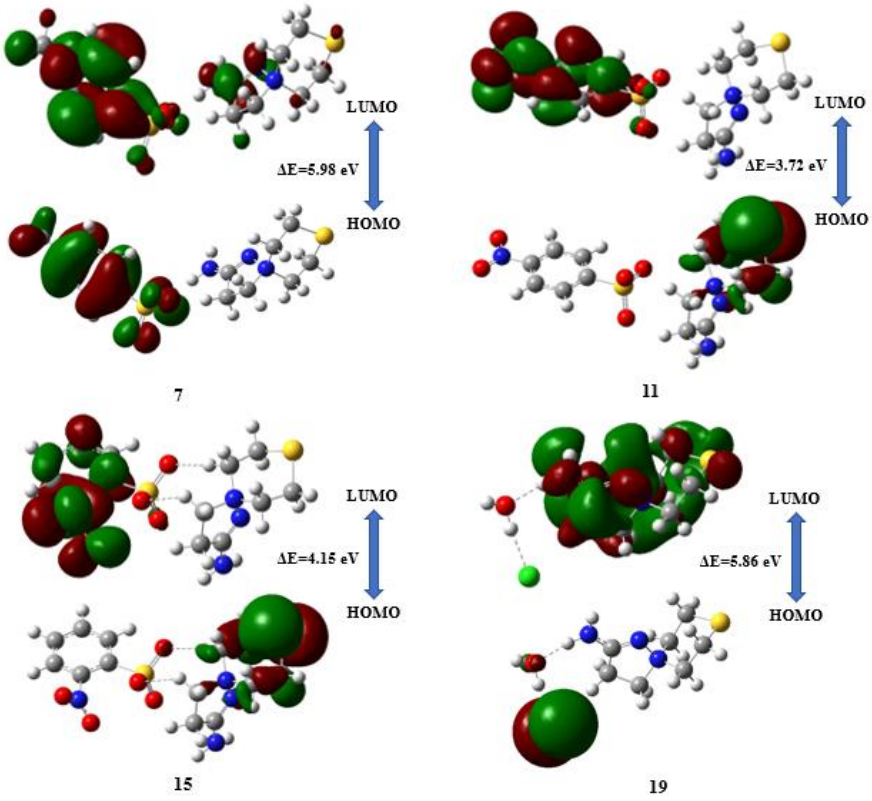


Figure 1 – Frontier molecular orbitals of products **7**, **11**, **15** and **19**.
Isovalue = 0.02.

A molecule with a high energy difference between HOMO and LUMO orbitals (energy gap) has low chemical reactivity and high kinetic stability [14]. Molecules with a high and low energy gap are called hard and soft molecules, respectively. Hard molecules are less polarizable than the soft ones and require more energy for excitation. Thus, it is clear from Table 2 that compounds **7** and **19** are less soft while **11** and **15** with relatively low energy gap are characterized by easy polarizability and high reactivity. Compound **11** having greater value of chemical potential (-4.88 eV) is the most reactive, while chloride monohydrate **19** is the least reactive (-3.54 eV) of all. A highest electron affinity value is found to be 3.02 in **11**. The least value of electron affinity is 0.61 observed in **19**. The NO_2 group in compounds **11** and **15** is a very strong electrophile; these compounds exhibit higher electrophilicity then **7** and **19**. The results of calculations show that the E(LUMO) orbitals of all the calculated structures are negative, which indicate that studied molecules are nucleophiles.

3. Experimental part

Methods for obtaining 2-amino-1,5-diazaspiro[4.5]dec-1-en-5-ium arylsulfonates, characteristics and identification were published in [1–3]. Conditions of 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate obtaining, its physical and chemical characteristics, NMR ^{1}H and ^{13}C spectra and X-ray diffraction data were given in [4].

The calculations were performed using Gaussian 09 package. The molecular structure of compounds was fully optimized using Density Functional Theory at the B3LYP levels with 6-31G++(d,p) basis set. The absence of imaginary (negative) frequencies in the calculation results indicates that a local minimum was found.

4. Conclusion

Calculations show that in most examples arylsulfonates are thermodynamically favorable, except when the initial substrate is β-(thiomorpholine-1-yl)propioamidoxime (**3**). 2-Amino-1,5-diazaspiro[4.5]dec-1-en-5-ium chloride monohydrate (**19**), based on comparing the values of Δ*G* reactions, is more advantageous compared to 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium tosylate, *para*-nitrophenylsulphonate and *ortho*-nitrophenylsulphonate (**7**, **11** and **15**, respectively). Thermodynamic calculations of the reactions of formation of product **18** compared to **6**, and product **20** compared to **8** are exceptions**.** The formation of monohydrate chloride **17** should be considered the least likely. The possibility of the formation of chloride monohydrates from arylsulfonates and hydrochlorides of DIPEA was also evaluated.

For 2-amino-8-thia-1,5-diazaspiro[4.5]dec-1-en-5-ium tosylate, *para*-nitrophenylsulphonate, *ortho*-nitrophenylsulphonate and chloride monohydrate the molecular orbitals were simulated and FMO comparative analysis was performed. The results of calculations show that all the E(HOMO) and E(LUMO) orbitals are negative, which indicate that studied molecules are stable.

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Conflicts of Interest: The authors declare no conflict of interest.

β-АМИНОПРОПИОАМИДОКСИМДЕРДІ АРИЛСУЛЬФОХЛОРЛАУДА 2-АМИНО-1,5-ДИАЗАСПИРО[4,5]ДЕЦ-1-ЕН-5-АММОНИЙ ХЛОРИД МОНОГИДРАТТАРЫНЫҢ ЖӘНЕ АРИЛСУЛЬФОНАТТАРЫНЫҢ ТҮЗІЛУІНДЕГІ БОС ЭНЕРГИЯЛАРЫ

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Түйіндеме. *Кіріспе.* Бұрын β-аминопропиоамидоксимдерді арилсульфохлорлау арқылы біз жаңа спиропиразолин қосылыстарын алдық. Бірақ белгілі бір жағдайларда β-(тиоморфолин-1-ил)пропиоамидоксимнің тозилденуінің негізгі немесе жанама өнімі 2-амино-8-тио-1,5-диазаспиро[4,5]дец-1-ен-5-аммония болатыны анықталды. Басқа β-аминопропиоамидоксимдер үшін тек 2-амино-1,5-диазаспиро[4,5]дец-1-ен-5-аммония арилсульфонаттары ғана бөлініп алынған. *Бұл жұмыстың мақсаты* β-аминопропиоамидоксимдердің тозилденуі, *пара*- және *орто*-нитробензолсульфохлорлану реакцияларын теориялық салыстыру және 2-амино-1,5-диазаспиро[4,5]дец-1-ен-5-аммоний хлориді моногидраттарының түзілу мүмкіндігін бағалау болып табылады. *Әдістемесі*. Барлық есептеулер Gaussian 09 бағдарламасын DFT/B3LYP/6-31G++(d,p) қолдана отырып жүргізілді. *Нәтижелер мен талқылау.* Термодинамикалық қолайлы өнімдер олардың түзілу реакцияларының Гиббстің бос энергияларын салыстыру арқылы анықталды. Есептелген ЖОМО және ТБМО энергияларына сүйене отырып, біз 2-амино-8-тио-1,5-диазаспиро[4,5]дец-1-ен-5-аммонийдің хлорид моногидраты, тозилатыны, *пара*-нитрофенилсульфонат пен *орто*-нитрофенилсульфонаттың химиялық тұрақтылығы мен реакция қабілеттілік параметрлерін болжадық. Бастапқы субстрат β-(тиоморфолин-1-ил) пропиоамидоксимді қоспағанда, көптеген жағдайларда арилсульфонаттар термодинамикалық тұрғыдан қолайлырақ. *Қорытынды.* 2-амино-8-тио-1,5-диазаспиро[4.5]дец-1-ен-5-аммоний хлоридінің моногидраты тиісті арилсульфонаттарға қарағанда тиімдірек.

Түйінді сөздер: β-аминопропиоамидоксимдер, арилсульфохлорлау, ТФТ әдісі, ЖОМО –ТБМО талдауы, Gaussian 09

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СВОБОДНЫЕ ЭНЕРГИИ ОБРАЗОВАНИЯ ХЛОРИДОВ МОНОГИДРАТОВ И АРИЛСУЛЬФОНАТОВ 2-АМИНО-1,5-ДИАЗАСПИРО[4,5]ДЕЦ-1-ЕН-5-АММОНИЯ ПРИ АРИЛСУЛЬФОХЛОРИРОВАНИИ β-АМИНОПРОПИОАМИДОКСИМОВ

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Резюме. *Введение.* Ранее при арилсульфохлорировании β-аминопропиоамидоксимов нами были получены новые спиропиразолиниевые соединения. Но было установлено, что при определенных условиях основным или побочным продуктом тозилирования β-(тиоморфолин-1-ил)пропиоамидоксима является моногидрат хлорида 2-амино-8-тио-1,5-диазаспиро[4,5]дец-1-ен-5-аммония. Для других β-аминопропиоамидоксимов были выделены только арилсульфонаты 2-амино-1,5-диазаспиро[4,5]дец-1-ен-5-аммония. *Цель настоящей работы* провести теоретическое сравнение реакций тозилирования, *пара*- и *орто*-нитробензолсульфохлорирования β-аминопропиоамидоксимов и оценить возможность образования моногидратов хлоридов 2-амино-1,5-диазаспиро[4,5]дец-1-ен-5-аммония. *Методология*. Расчеты выполнены с использованием пакета Gaussian 09 методом DFT/B3LYP/6-31G++(d,p). *Результаты и обсуждение.* Термодинамически предпочтительные продукты идентифицировали путем сравнения свободных энергий Гиббса реакций их образования. На основе рассчитанных энергий ВЗМО и НСМО было выполнено прогнозирование параметров химической стабильности и реакционной способности для моногидрата хлорида, тозилата, *пара*-нитрофенилсульфоната и *орто*-нитрофенилсульфоната 2-амино-8-тио-1,5-диазаспиро[4,5]дец-1-ен-5-аммония. В большинстве случаев арилсульфонаты термодинамически более выгодны, за исключением случаев, когда исходным субстратом является

β-(тиоморфолин-1-ил)пропиоамидоксим. *Заключение.* Моногидрат хлорида 2-амино-8-тио-1,5-диазаспиро[4.5]дец-1-ен-5-аммония более предпочтителен по сравнению с соответствующими арилсульфонатами.

Ключевые слова: β-аминопропиоамидоксимы, арилсульфохлорирование, метод ТФП, анализ ВЗМО–НСМО, Gaussian 09

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