Quantum chemical study of the electronic structure and reactivity of complexes of 4-oxo-4-(2-thienyl)- and 4-(5-methyl-2thienyl)-4-oxobutyryl chlorides with aluminum chloride*

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The geometry and electronic structures of complexes of 4-oxo-4-(2-thienyl)- and 4-oxo-4-(5-methyl-2-thienyl)butyryl chlorides with aluminum chloride, as well as the corresponding carbocations, were studied in terms of the density functional theory (DFT) using the B3LIP/6-311+G(2d,p) method and the semiempirical PM6 method. An analysis of the relative energies of the complexes and cations made it possible to interpret side reactions accompanying the acylation of thiophenes with succinyl dichloride.

Key words: quantum chemical calculations, PM6 method, density functional theory (DFT), B3LYP functional, electrophilic substitution.

1,4-Di(2-thienyl)butane-1,4-diones are key compounds in the synthesis of 2,5-di(2-thienyl)pyrroles, 2,5di(2-thienyl)furans, and the corresponding 2,2':5',2"-terthiophenes (terthienyls), which are actively studied and used in the recent years for the preparation of organic polymers and semiconductors (see review¹). A number of methods for synthesis of 1,4-di(2-thienyl)butane-1,4-diones is described, and the most part of them is multistage (if starting from the corresponding thiophenes). In our opinion, the most promising method for the synthesis of 1,4-dithienylbutane-1,4-diones is the one-stage acylation of the corresponding thiophenes with succinyl chloride.

However, this reaction under the standard (for compounds of the thiophene series) conditions, *i.e.*, using $SnCl_4$ as a condensing agent, after usual treatment affords only the monoacylation product: 4-oxo-4-(2-thienyl)-butyric acid.² 1,4-Di(2-thienyl)butane-1,4-dione has successfully been obtained for the first time from thiophene and succinyl chloride by acylation in the presence of aluminum chloride.³ Nevertheless, the yields of target diketones almost never exceeded 50% of the theoretical value.^{4,5} We studied⁵ reasons for such modest yields.

The reactions of thiophene and 2-methyl- and 2-bromothiophenes (1a-c) with succinyl dichloride in the presence of AlCl₃, TiCl₄, and SnCl₄, which proceed, evidently, through complexes of ketoacid chlorides $2\mathbf{a}-\mathbf{c}$ with Lewis acids, were considered.⁵ The influence of the Friedel—Crafts acylation conditions and the relative amount and nature of the Lewis acid on the ratio and yields of formed 1,4-di(2-thienyl)-1,4-diones $3\mathbf{a}-\mathbf{c}$ and 4-oxo-4-(2-thienyl)butyric acids $4\mathbf{a}-\mathbf{c}$ was shown. The earlier unknown direction of transformations in the system thiophene compound—succinyl dichloride—AlCl₃ was found and its products were isolated: 4,4-di(2-thienyl)but-3-enoic acids $5\mathbf{a}-\mathbf{c}$, whose formation can easily be presented as a result of alkylation of thiophene $1\mathbf{a}-\mathbf{c}$ involving the keto group of acid chloride $2\mathbf{a}-\mathbf{c}$ or acid $4\mathbf{a}-\mathbf{c}$ followed by dehydration.

The ability of acids $5\mathbf{a}-\mathbf{c}$ to ring-chain tautomerism, which is known for the benzene analogs, makes it possible to explain the presence (discovered in Ref. 5) of 4,4-di(2thienyl)-substituted γ -butyrolactones $6\mathbf{a}-\mathbf{c}$ in mixtures of the reaction products (Scheme 1). Another possible route for the formation of lactones 6 was considered.⁶ This route includes consecutive transformations of acid chlorides 2 into acylium cations 7 and cyclization of the latter into carbocations 8, whose reaction with thiophenes 1 can result in the formation of compounds 6 without an intermediate formation of unsaturated acids 5 (Scheme 1).

According to Scheme 1, the first stage of the processes discussed is common for the formation of both target products (diketones of type 3) and by-products 4-6. This stage of a classical Friedel—Crafts acylation results

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^{*} Dedicated to the Academician of the Russian Academy of Sciences I. P. Beletskaya on the occasion of her birthday.



Scheme 1

R = H(a), Me (b), Br (c)

(after usual treatment of the reaction mixture) in the expected keto acids of type 4. Substantial distinctions are observed at the second stage. They are due to different transformations of intermediates, acid chlorides 2 (in the form of complexes with AlCl₃): diketones 3 are formed in the standard reaction with the second molecule of thiophene compound 1 and require the participation of an nv-complex in which the AlCl₃ molecule is bound to the Cl atom or the O atom of the chlorocarbonyl group (this nv-complex can be considered as a precursor of the corresponding acylium ion), while the formation of unsaturated acids of type 5 assumes the intermediate formation of hydroxy acid 9 due to the alkylation of thiophene involving a complex of acid chloride 2 with AlCl₃ at the O atom of the carbonyl group. Finally, lactones of type 6 can be formed either by the intramolecular addition of COOH group to the C=CH bond of acids 5, or through the intramolecular O-acylation of acid chloride 2 accompanied by the attack of the formed cation 8 (counterion $AlCl_4^-$ is omitted in Scheme 1) to the second molecule of thiophene or its derivative.

Results and Discussion

In this work, the quantum chemical study of the isomeric nv-complexes of acid chlorides **2a** and **2b** with aluminum chloride, *viz.*, compounds **10a,b**—**12a,b**, was performed in terms of the density functional theory (DFT) using the B3LYP hybrid functional by the B3LYP/6-311+G(2d,p) method and in the PM6 semiempirical approximation.



The results of this study allow one to conclude about the preferential localization of the AlCl₃ molecule at one of the carbonyl O atoms or at the Cl atom. The bond lengths calculated by both methods almost coincide and agree with the known data on bond lengths in compounds of diverse elements, including ordinary C–C bonds between atoms with different hybridization (C_{sp3} – C_{sp3} , C_{sp2} – C_{sp2} , C_{sp2} – C_{sp2}), which are present in objects of our

Table 1. Selected bond lengths (*d*) in complexes 10a,b-12a,b calculated by the B3LYP/6-311+G(2d,p) method

Bond	d/Å							
	10a	10b	11a	11b	12a	12b		
C(1)–C(2)	1.47	1.48	1.49	1.49	1.51	1.51		
C(1) - O(1)	1.15	1.15	1.22	1.22	1.18	1.18		
C(2) - C(3)	1.54	1.52	1.52	1.53	1.55	1.54		
C(3) - C(4)	1.53	1.53	1.53	1.53	1.50	1.51		
C(4) - C(5)	1.46	1.45	1.46	1.46	1.43	1.42		
C(4) - O(2)	1.22	1.22	1.22	1.22	1.26	1.26		
C(1) - Cl(1)	2.12	2.14	1.75	1.75	1.82	1.82		
Al-O(1)	_	_	1.94	1.94	_	_		
Al-O(2)	_	_	_	_	1.87	1.87		
Al-Cl(1)	2.24	2.37	_	_	_	_		
Al-Cl(2)	2.14	2.13	2.12	2.12	2.14	2.13		
Al-Cl(3)	2.11	2.13	2.13	2.11	2.12	2.12		
Al-Cl(4)	2.01	2.11	2.13	2.13	2.14	2.14		

study.⁷ At the same time, some values of bond and dihedral angles calculated by the PM6 method noticeably differ from those obtained by the more perfect B3LYP/6-311+G(2d,p) method.

Therefore, in further considerations of the calculated structural and energy characteristics, we used only the

results obtained by the B3LYP/6-311+G(2d,p) method. As shown,^{8,9} reliable calculations of geometric and energy parameters are possible in terms of the DFT method when using the B3LYP hybrid functional for five-membered heterocyclic compounds with one heteroatom. These calculations make it possible to interpret the reactivity of the compounds, particularly, the directivity of the electrophilic substitution reactions.

The structural characteristics of the most important (in the framework of the present study) fragments of compounds 10a,b-12a,b, *viz.*, aliphatic chains Cl-C(O)-CH₂-CH₂-C(O)- including the C(4)-C(5) bond and bonds of coordinated AlCl₃ molecules, calculated by the B3LYP/6-311+G(2d,p) method are presented in Tables 1-3. The C-H bond lengths ranging, in all cases, from 1.08 to 1.10 Å are omitted. Tables 2 and 3 include the bond and dihedral angles that characterize the geometric and conformational peculiarities of these aliphatic fragments.

A characteristic feature of complexes 10a,b and 11a,bis an almost planar zigzag conformation of the C(1)-C(2)-C(3)-C(4)-C(5) chain, and the O(1)-C(1)-Cl(1)-Al and C(1)-O(1)-Al-Cl(2) fragments substantially deviate from the plane of this carbon chain. On the contrary, in complexes 12a,b the C(1)-C(2)-C(3)-C(4)-C(5) chain does not lie in one plane, which is un-

Table 2. Bond angles (ω) in complexes **10a**,**b**–**12a**,**b** calculated by the B3LYP/6-311+G(2d,p) method

Angle			ω/	deg			Angle	ω/deg			
	10a	10b	11a	11b	12a	12b		11a	11b	12a	
O(1) - C(1) - Cl(1)	110.3	113.1	116.4	116.3	120.7	120.6	C(1)-O(1)-Al	137.3	137.6	_	
O(1) - C(1) - C(2)	139.0	139.9	124.6	124.6	126.4	124.5	O(1)-Al-Cl(2)	102.6	102.7	_	
Cl(1) - C(1) - C(2)	110.7	106.8	119.0	119.0	120.7	112.9	O(1)-Al-Cl(3)	100.8	100.8	_	
O(2) - C(4) - C(3)	120.2	120.2	120.7	120.7	121.3	121.0	O(1)-Al-Cl(4)	100.8	100.8	_	
O(2) - C(4) - C(5)	122.3	122.7	121.9	122.0	118.0	118.1	C(4) - O(2) - Al	_	_	141.5	
C(1)-Cl(1)-Al	121.6	126.6	_	_	_	_	O(2)-Al-Cl(2)	_	_	103.1	
Cl(1)- Al - $Cl(2)$	103.7	102.2	_	_	_	_	O(2)-Al-Cl(3)	_	_	102.8	
Cl(1)- Al - $Cl(3)$	100.2	102.9	_	_	_	_	O(2)-Al-Cl(4)	_	_	104.2	
Cl(1)- Al - $Cl(4)$	103.2	102.2	_	_	_	_					

Table 3. Selected dihedral angles (ϕ) in complexes 10a,b-12a,b calculated by the B3LYP/6-311+G(2d,p) method

Angle	φ/deg		Angle	φ/deg		Angle	φ/deg	
	10a	10b		11a	11b		12a	12b
$\overline{O(1)-C(1)-Cl(1)-Al}$	169.2	83.8	C(2)-C(1)-O(1)-Al	0.0	0.0	C(5)-C(4)-O(2)-Al	172.6	172.8
C(2)-C(1)-Cl(1)-Al	-10.4	-99.4	C(1) - O(1) - Al - Cl(2)	180.0	180.0	C(4) - O(2) - Al - Cl(2)	73.5	-43.5
C(1)-Cl(1)-Al-Cl(2)	44.8	104.4	C(1) - O(1) - Al - Cl(3)	-59.3	-59.4	C(4) - O(2) - Al - Cl(3)	-166.5	103.5
C(1)-Cl(1)-Al-Cl(3)	166.1	-134.6	C(1) - O(1) - Al - Cl(4)	59.4	59.4	C(4) - O(2) - Al - Cl(4)	-46.0	-163.8
C(1)-Cl(1)-Al-Cl(4)	-73.6	-12.7	O(2) - C(4) - C(5) - C(6)	180.0	180.0	O(2) - C(4) - C(5) - C(6)	179.3	79.3
C(1)-C(2)-C(3)-C(4)	160.6	175.5	C(1)-C(2)-C(3)-C(4)	180.0	180.0	C(1)-C(2)-C(3)-C(4)	167.9	92.1
C(2)-C(3)-C(4)-C(5)	160.8	176.9	C(2)-C(3)-C(4)-C(5)	180.0	180.0	C(2)-C(3)-C(4)-C(5)	92.1	95.7
O(2) - C(4) - C(5) - C(6)	175.6	177.6				., ., ., .,		

ambiguously a consequence of steric effect caused by the presence of the bulky residue AlCl₃.

We also calculated "open" carbocations 7a,b, which can be considered as intermediates in the synthesis of target diketones 3a,b, and "closed" cations 8a,b, which are possible intermediates in the formation of unsaturated acids 5a,b and lactones 6a,b (Table 4).



It should be mentioned that in "open" cations 7a,b the C(2)-C(3)-C(4)-C(5) fragment lies as a zigzag in nearly one plane, whereas the O(1)-C(1) bond is approximately perpendicular to the plane of zigzag. In "closed" cations 8a,b two five-membered rings are almost coplanar.

As should be expected according to published data,⁸ it is difficult to interpret the calculated charges on atoms.

The relative energies (ΔE) of complexes 10–12 and cations 7 and 8 calculated by the B3LYP/6-311+G(2d,p) method are given in Table 5. An analysis of these energies made it possible to interpret side reactions accompanying the acylation of thiophenes with succinyl dichloride. Note that the PM6 method gives close values of relative energies.

Table 4. Selected bond lengths (*d*) and bond (ω) and dihedral (φ) angles in cations **7a**,**b**–**8a**,**b** calculated by the B3LYP/6-311+G(2d,p) method

Parameter	7a	7b	8 a	8b			
Bond	d/Å						
C(1) - O(1)	1.21	1.12	1.16	1.17			
C(1)-O(2)	_	_	1.50	1.49			
C(1) - C(2)	1.42	1.40	1.50	1.51			
C(4)—O(2)	1.22	1.23	1.53	1.53			
C(2)-C(3)	1.55	1.55	1.28	1.31			
C(3)—C(4)	1.55	1.55	1.50	1.51			
C(4) - C(5)	1.44	1.43	1.39	1.38			
Angle		α	o/deg				
O(1) - C(1) - C(2)	178.2	178.5	135.4	134.7			
C(1) - C(2) - C(3)	114.5	114.6	105.9	105.7			
C(2) - C(3) - C(4)	105.0	104.7	104.3	104.1			
O(2) - C(4) - C(3)	117.5	117.2	112.9	112.6			
O(2) - C(4) - C(5)	123.6	124.4	119.4	119.5			
C(1) - O(2) - C(4)	—	_	110.9	111.0			
		¢	/deg				
O(1) - C(1) - C(2) - C(3)	-83.6	85.7	-179.9	-180.0			
C(1)-C(2)-C(3)-C(4)	134.1	-132.2	0.0	0.0			
C(2) - C(3) - C(4) - C(5)	170.0	-170.8	180.0	-180.0			
O(2)-C(4)-C(5)-C(6)	-1.0	179.9	0.0	0.0			

Table 5. Total (E_{tot}) and relative (E_{rel}) energies of cations **7a,b** and **8a,b** and complexes **10a,b–12a,b** (R = H(a), Me(b)) calculated by the B3LYP/6-311+G(2d,p) method

Compound	$\Delta E_{\rm rel}/\rm kcal~mol^{-1}$	$\Delta E_{\rm tot}/{\rm Hartree}$
7a	28.58	_
7b	29.67	_
8a	0	-857.60429
8b	0	-896.94324
10a	18.78	_
10b	19.43	_
11a	10.38	_
11b	11.69	_
12a	0	-2941.48902
12b	0	-2980.82294

Among complexes 10a,b-12a,b, forms 12a,b with AlCl₃ molecule localization at the carbonyl O atom of the ketone groups are energetically preferential rather than their isomers 10a,b and 11a,b, in which the AlCl₃ molecule is bound to the Cl atom or the O atom of the chlorocarbonyl group. Similarly, among cations 7 and 8, not open forms 7a,b but their closed isomers 8a,b, in which the positive charge is localized on the C(4) atom of the lactone cycle, are preferable. These are complexes 12 and cations 8 which are natural intermediates in the synthesis of "anomalous" products, unsaturated acids 5 and lactones 6 (see Scheme 1).

By considering possible transformations in the system thiophene compound-succinyl dichloride-AlCl₃ presented in Scheme 1, one can explain remained unclear low yield of diketone 3b from the most active of model substrates, 2-methylthiophene, compared to diketones 3a,c formed from less reactive thiophene and 2-bromothiophene: it is enough to assume that the alkylation reactions $2 \rightarrow 5$ and $2 \rightarrow 6$ are accelerated, in the case of reactive methylthiophene, to a greater extent than acylation $2 \rightarrow 3$. Indeed, it is easily seen from published data⁵ that 0.7 mole of acid 5a and lactone 6a (totally) and 0.2 mole of acid 5c are formed from thiophene and 2-bromothiophene per 1 mole of diketones 3a and 3c under the same conditions optimum for the preparation of diketones (molar ratio AlCl₃: succinyl chloride = 6, temperature 40 °C, reaction time 12 h), whereas in the case of 2-methylthiophene the amount of acids and lactones attains already 1.2 moles per 1 mole of diketone 3b. Note that this is the enhanced (over other thiophenes) formation of unsaturated acid from 2-methylthiophene that made it possible to identify acid 5b in the mixture and also isolate it in the individual state.⁵

Since the total yields of compounds of type 3, 5, and 6 range from 65 to 79%, we cannot rule out the possibility of formation, under the reaction conditions, of other byproducts that can be formed first of all from acids 5 or their chlorides and from lactones 6. Similar transformations leading to 4-phenyl-1-naphthol are well known



Conditions: *i*. PCl₃ or Δ ; *ii*. PCl₃ or Ac₂O.

for the benzene analogs according to Borsche's data¹⁰ (Scheme 2) and can easily be interpreted as a result of intramolecular acylation. The transformation of 4,4-diphenylbutyrolactone described in the same article is evidently the result of the above mentioned ring-chain tautomerism between lactone and unsaturated acid. In work,¹¹ 4,4-diphenylbut-3-enoic acid or its ethyl ester was transformed into 4-phenyl-1-naphthol by the action of zinc chloride. At the same time, it should be kept in mind that the high reactivity of thiophenes can yield polycondensation (resinification) products under drastic conditions.

Finally, let us consider the factors that prevent the second stage of the reaction to occur, *i.e.*, acylation of thiophenes 1a-c with 4-oxo-4-thienylbutyryl chlorides 2a-c in the presence of Lewis acids of medium strength, such as tin and titanium tetrachlorides, but allow this acylation to occur in the presence of a stronger acid, aluminum chloride. An apparently similar situation is observed when thiophenes react with α -haloalkanoic acid chlorides, in particular, chrloroacetyl chloride.

It was shown¹² that chloroacetyl chloride, which is a weaker base than alkanoyl chlorides, does not almost form an nv-complex with tin tetrachloride and, therefore, requires to use a stronger Lewis acid, aluminum chloride. The necessity to perform acylation of alkylthiophenes in the presence of $AlCl_3$ in the case of oxalyl chloride^{13,14} and squaric acid dichloride^{15,16} was explained similarly. A similar explanation is natural for compounds in which the basicity of the chlorocarbonyl group can decrease because of the negative inductive and/or resonance effects of the adjacent substituent but does not appropriate for the interpretation of the behavior of succinyl chloride, since in its molecule the electron-withdrawing groups are separated by the dimethylene fragment and, in addition, the first stage of acylation proceeds normally in the presence of SnCl₄ and TiCl₄.

Based on the results of quantum chemical calculations performed in this work, in particular, on the geometric characteristics of complexes **12a**,**b**, one can assume that the second acylation stage is impeded by steric factors: shielding of the chlorocarbonyl group with the Lewis acid bound in a complex at the carbonyl group. Note that, unlike aluminum chloride, compounds of tetravalent tin and titanium are capable of forming complexes with the coordination number 6; *i.e.*, in the considered cases, we cannot exclude the formation of a seven-membered complex in which the MCl_4 molecule accept as ligands two carbonyl groups belonging to the same succinyl dichloride molecule.

In connection to the aforesaid, we should consider changes in the behavior of acid dichlorides $ClCO(CH_2)_{\mu}COCl$ with an elongation of the distance between the chlorocarbonyl groups. The formation of 5,5-di-(2-thienyl)pentane-1,5-dione under the Friedel-Crafts conditions has first been described¹⁷ in 1955. This diketone was isolated in a yield of 5% when ethyl 4-(2-thenoyl)butyrate was distilled, which was explained by the presence of an admixture of glutaryl dichloride in the acylating agent (half-ester of glutaryl chloride). It should be mentioned that almost the same yield of diketone was obtained by us under similar conditions (see Experimental) when using glutaryl dichloride, and the major identified product was 4-(2-thenoyl)butyric acid, i.e., glutarodichloride and succinodichloride strongly resemble each other in behavior in the presence of tin tetrachloride.

However, whether the article¹⁷ remained unnoticed or its results did not inspired other chemists, but no description of the synthesis of 1,5-(2-thienyl)pentane-1,5-dione by the reaction of glutarodichloride with thiophene was found during almost subsequent 60 years, although syntheses of this diketone by other methods were carried out,^{18–20} as well as the Friedel—Crafts syntheses in the presence of AlCl₃, in which substituted 1,5-bis(3-thienyl)pentane-1,5-diones successfully used as intermediates for the preparation of photochromic dithienylethenes were obtained in high yields.^{21,22}

The situation is substantially different for adipodichloride, which smoothly acylates thiophene in the presence of tin tetrachloride to form 1,6-di(2-thienyl)hexane-1,6-dione (83% yield).²³ There are data²⁴ on thiophene acylation with succinic anhydride and polyanhydride of higher dicarboxylic acids HOOC(CH₂)_nCOOH, n = 4, 6–8 in the presence of SnCl₄. In the case of succinic anhydride and adipinic polyanhydride, only the corresponding keto acids were obtained, which is quite expectable for anhydrides. On the contrary, both keto acids and diketones are formed from polyanhydrides of higher dicarboxylic acids (n = 6-8), which is difficult for interpretation.

Thus, side reactions that accompany the acylation of thiophenes with succinyl dichloride were interpreted by the quantum chemical calculations. The energy preference of nv-complexes with aluminum chloride at the ketone carbonyl group in the intermediate formed at the first stage of acylation, 4-oxo-4-(2-thienyl)butyryl chloride, was shown. This should favor the formation of by-products: 4,4-dithienylbut-3-enoic acids and 4,4-di(2-thienyl)-substituted y-butyrolactones. The reactions of succinyl, glutaryl, and adipinyl chlorides with thiophene were compared. The results of the comparison do not contradict our assumption about the steric shielding of the chlorocarbonyl group in 4-oxo-4-(2-thienyl)butyryl chloride, with the SnCl₄ or TiCl₄ complex at the ketone group of the same acid chloride. A similar effect is manifested by glutaryl chloride and is absent for adipinyl chloride.

Calculation and Experimental Procedures

Quantum chemical calculations in the semiempirical PM6 approximation were performed using the published program.²⁵ The DFT calculations were performed by the B3LYP/6-311+G(2d,p) method using the GAUSSIAN-09 program package.²⁶

Acylation of thiophene with glutaryl dichloride. A solution of glutaryl dichloride (18.5 g, 0.11 mol) in benzene (50 mL) was added dropwise within 2 h at 0-3 °C to a solution of thiophene (15 g, 0.18 mol) and SnCl₄ (46 g, 22 mL, 0.18 mol) in benzene (200 mL). Then the mixture was treated with hydrochloric acid (1 : 10) at 10 °C and washed with a solution of Na₂CO₃ and water. Benzene was distilled off. The residue was recrystallized from butyl acetate. 1,5-Di(2-thienyl)pentane-1,5-dione was obtained in a yield of 1.2 g (5.3%), m.p. 88–89 °C (*cf.* Ref. 17: m.p. 88.5 °C). The acidification of the alkaline extract gave 5 g (27% yield) of 5-oxo-5-(2-thienyl)valeric acid, m.p. (*cf.* Ref. 17: m.p. 92 °C).

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