REACTIONS OF TOLUIDINE ISOMERS WITH OXALIC, MALONIC, AND SUCCINIC ACIDS

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Abstract: *This paper investigates alternative conditions for synthesizing salts and toluidides of toluidine isomers with oxalic acid, malonic, and succinic acids. In these syntheses, the salt formation reactions of toluidines with oxalic acid in a 2:1 molar ratio and with malonic and succinic acids in a 1:1 molar ratio at room temperature in ethanol for 30 minutes to 7 days, and for the synthesis of amide-linked compounds, heating in toluene for 3 hours, were shown as alternative conditions. The structure of the obtained compounds was studied using modern physicochemical research methods such as IR spectrum, PMR analysis, and X-ray analysis.*
Keywords: *toluidine isomers, oxalic acid, malonic acid, succinic acid, quaternary salt and toluidine, IR-spectrum, ^{1}H NMR and X-ray analysis.*

Introduction

It is known from the literature that the vast majority of compounds obtained by the reaction of aromatic amines with carboxylic acids exhibit high biological activity. This can be attributed to the high water solubility of the quaternary ammonium salts and amide-linked compounds with various functional groups, and the presence of various element atoms in the molecule [1]. The amide group is a widely prevalent functional group found in the structures of many physiologically active synthetic and natural molecules, as well as biopolymers [2]. The reactions of saturated monobasic carboxylic acids with functionally substituted primary aromatic amines (3-amino-2-naphthol, benzo[d]thiazol-2-amine, and 4,4′-oxydianiline) in the presence of $TaCl_5$ selectively yield carboxylic acid amides with diverse structures. A mechanism for the amidation of carboxylic acids facilitated by $TaCl_5$ has been proposed [3].

Amide bond formation is among the most commonly used reactions in the synthesis of natural products, pharmaceuticals, and fine chemicals. A survey found that over 25% of known drugs contain amide groups. Traditionally, amides were syntheses through the condensation of carboxylic acids and amines. The use of coupling reagents typically ensures mild reaction conditions and high yields [4].

The reaction of N-arylacetoacetamides with aromatic aldehydes in the presence of piperidine and ethanol produced N,N′,2-triaryl-6-hydroxy-6-methyl-4-oxocyclohexane-1,3-dicarboxamides. These compounds further reacted with p-toluidine, yielding dehydration products. Additionally, reactions of N,N′,2-triaryl-6-hydroxy-6-methyl-4-oxocyclohexane-1,3-dicarboxamides with hydrazine hydrate and cyanoacetic acid hydrazide led to the formation of tetrahydroindazoles [5].

The reaction of 6-methylpyridin-2-ylphosphine with benzaldehyde and p-toluidine was studied, resulting in the formation of three isomers of acyclic aminomethylphosphine oxide with moderate yield [6, 7]. Amide-linked compounds are widely used in medicine because they have high activity, good water solubility or are easy to convert to a water-soluble state. Oxyphenamide - para-oxyphenylsalicylamide and paracetamol - para-acetamidophenol is among them. The analysis of literature data showed that the reactions of aromatic amines with carboxylic acids were not systematically studied, initially attention was not paid to studying the structure of aromatic amines and carboxylic acids.

Researchers from the National University of Uzbekistan conducted the salt formation reactions of aromatic amines with carboxylic acids in ethanol, and the amide-linked compounds in toluene or xylenes, obtaining products in high yields [8,9]. Studies have shown that quaternary ammonium salts, which are initially formed by the reaction of amines with carboxylic acids, have different structures, as determined by X-ray diffraction analysis [10-12].

The aim of the present work is studying the obtaining of the salts of toluidine isomers with relatively high acidity, such as oxalic acid, malonic, and succinic acids, and analyze their structure.

Experimental part

Materials. In this research work, toluidine isomers, oxalic acid, malonic, succinic acids, and other substances were used. These substances were purchased in "chemically pure" form from Merit Chemical.

Methods. *IR-analysis.* The IR spectra of these synthesized ammonium toluidine salts and toluidites were obtained in the range of 400-4000 cm^{-1} in the form of tablets with potassium bromide on a Sistem-2000 FT-IR spectrophotometer.

NMR and PMR analysis. The structure of the resulting chemical compounds was determined by ^{1}H NMR spectra in $(CD_3)_2SO+CCl_4$ solutions on a UNITY 400+/ICPS spectrometer with an operating frequency of 400 MHz

The X-ray diffraction analysis of the obtained ammonium toluidine salts was studied on an “Xcalibur” diffractometer from the Oxford Diffraction company.

Synthesis. *Preparation of salts of isomeric toluidines with oxalic, malonic and succinic acids.* A solution of isomer toluidine in ethanol with a molar ratio of 2:1 with oxalic acid and 2:1 with malonic and succinic acids in ethanol was added to the beaker and left at room temperature for 30 minutes. The resulting crystals were dried in a calcium chloride desiccator and washed with ethanol.

Preparation of toluidine isomers with formic acid, malonic, and succinic acids toluidine. Toluidine isomer and dicarboxylic acid were placed in a round-bottomed flask equipped with a reflux condenser and a water separator in a 2:1 molar ratio, toluene was added and boiled for 3 hours. Then the toluene was distilled. The remaining liquid mass was dried in a calcium chloride desiccator. It was recrystallized from toluene.

Table 1. Dependence of the molar ratio of the starting materials on the yield of the reactions for the synthesis of ammonium toluidine salts (solvent - ethanol, temperature 25 ^{0}C)

Aromatic amine	Dicarbonic acid	Mol ratio	Yield, %	Mol ratio	Yield, %
o-toluidine	Oxalic acid	1:1	47	2:1	91
o-toluidine	Malon acid	1:1	95	2:1	89
o-toluidine	Succinicacids	1:1	97	2:1	91

Taking into account the presence of two carboxyl groups in the oxalic acid, the reactions were carried out in 1:1 and 2:1 molar ratios. Initially, the reaction of o-toluidine with oxalic acid at room temperature in 1:1 and 2:1 molar ratios, in ethanol, yielded products with the same melting point.

Considering that the IR spectra of the salts obtained as a result of the reactions of o-toluidine with oxalic acid in 1:1 and 2:1 molar ratios are the same, and the IR spectrum does not show absorption bands specific to the unreacted carboxyl group, it was concluded that a 1:1 salt was formed in this reaction.

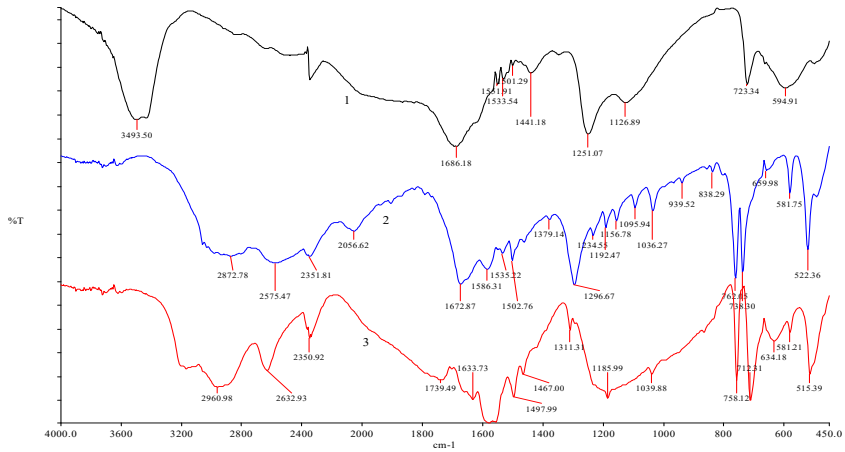
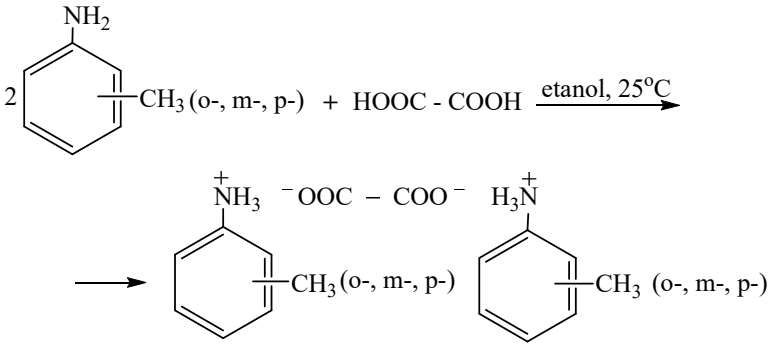


Fig. 1. Comparison of IR spectra of (**1**) oxalic acid, (**2**) di-(2-methylphenylammonium) oxalate, (**3**) formic acid di-(2-methylphenyl)amide

The above and the fact that the yield of the product in the 1:1 molar ratio reaction did not exceed 50% (Table 1) indicate that this reaction reacted with two carboxyl groups in a 2:1 ratio. As a result of the reaction, salts of ortho-, meta- and para-toluidines with oxalic acid - di-(X-methylphenylammonium) oxalate (X=2, 3, 4) salts were obtained in 91, 95 and 97% yields (Scheme 1):



Scheme 1. Salt formation reactions of toluidine isomers with oxalic acid

Both the 1:1 and 2:1 molar ratios of malonic acid to salt formation reactions yielded products with the same melting point. The IR spectra of both reaction products showed absorption bands characteristic of the unreacted carboxyl group (Fig. 2).

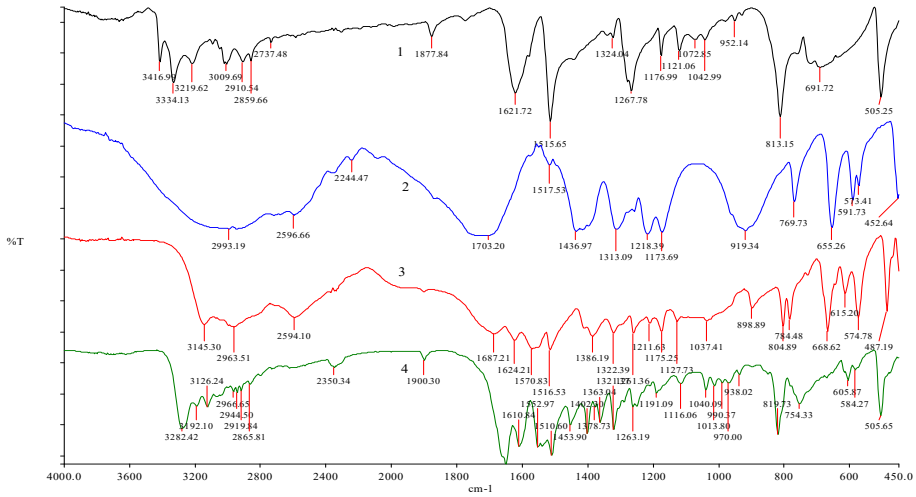


Fig. 2. Comparison of IR spectra of (**1**) m-toluidine, (**2**) malonic acid, (**3**) mono-(3-methylphenylammonium)malonate, (**4**) di-(3-methylphenyl)amide of malonic acid

In order to clarify our findings, we grew single crystals of the products obtained from the above reactions. X-ray diffraction analysis showed that the resulting salt was composed of a 1:1 molar ratio (Figure 3) and was hydrogen bonded to each other (Figure 4).

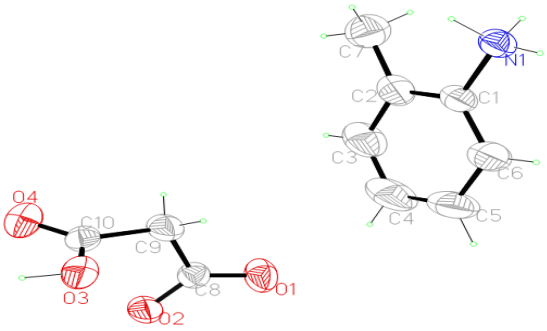


Fig. 3. Spatial structure of mono-(2-methylphenylammonia) malonate

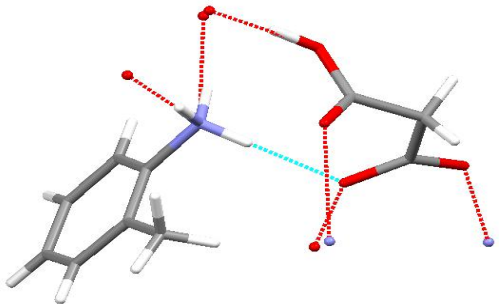
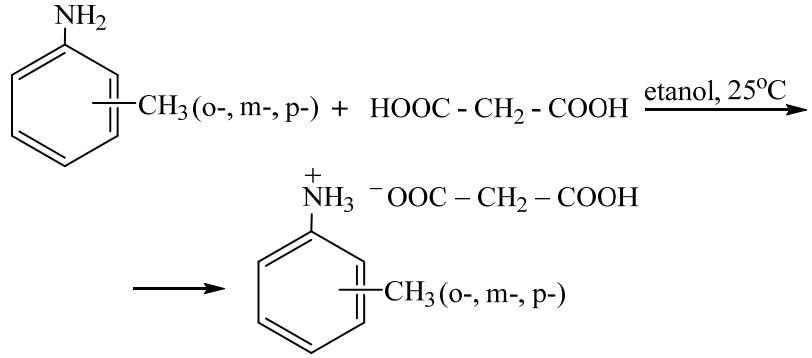


Fig. 4. Hydrogen bonds in the molecule mono-(2-methylphenylammonia) malonate

The reactions of toluidine isomers with malonic acid in ethanol at room temperature gave the corresponding mono-(X-methylphenylammonium) malonates (X=2, 3, 4) in 87, 91, and 93% yields (Scheme 2):



Scheme 2. Salt formation reactions of toluidine isomers with malonic acid

The results of X-ray structural analysis maintain that the salt obtained from the reaction of malonic acid with p-toluidine is formed in a 1:1 molar ratio (Fig.s 5 and 6):

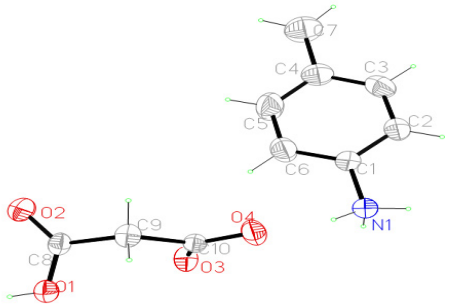


Fig. 5. Spatial structure of mono-(4-methylphenyl-ammonium) malonate

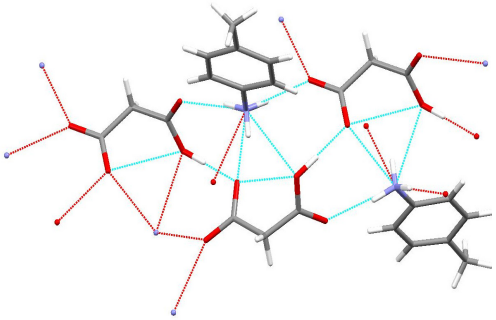
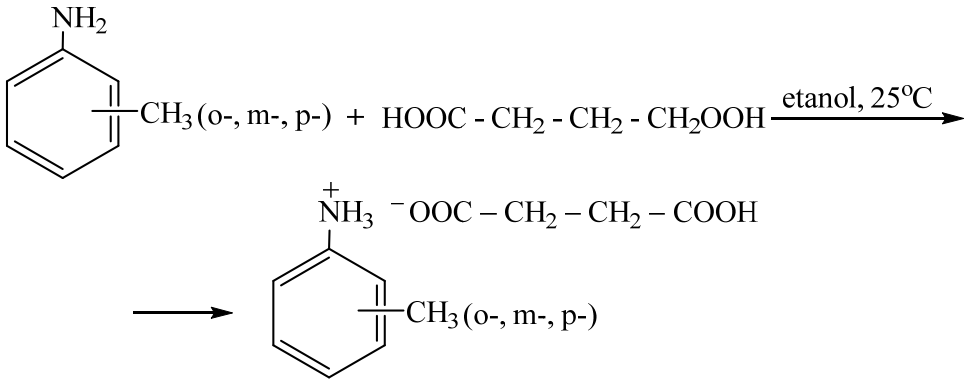


Fig. 6. Hydrogen bonds in the molecule of mono-(4-methylphenyl-ammonium) malonate

We isolated a single crystal of the product obtained from the reaction of p-toluidine with succinic acid in ethanol at room temperature. X-ray diffraction analysis confirmed that this salt was also composed of p-toluidine and succinic acid in a 1:1 molar ratio (Fig.s 7 and 8). As a result of the

reactions carried out in ethanol at room temperature, the corresponding salts of o-, m- and p-toluidines with succinic acid were obtained in 88, 89 and 91% yields (Scheme 3):



Scheme 3. Salt formation reactions of toluidine isomers with succinic acid

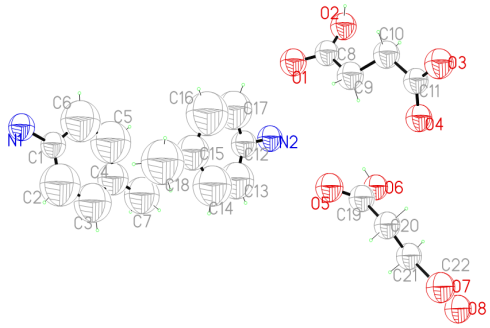


Fig. 7. Spatial structure of mono-(4-methylphenylammonium) succinate

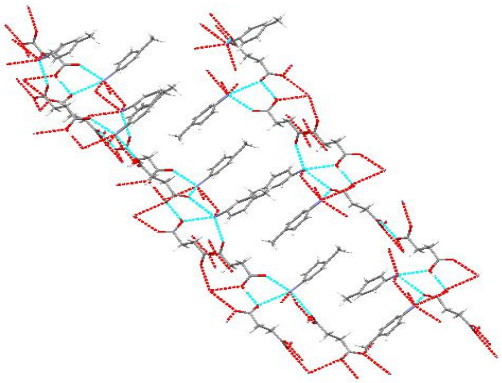
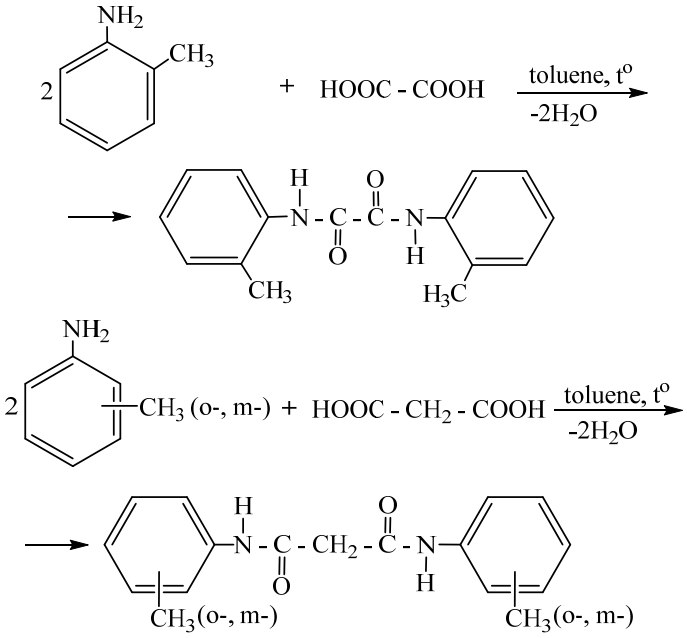
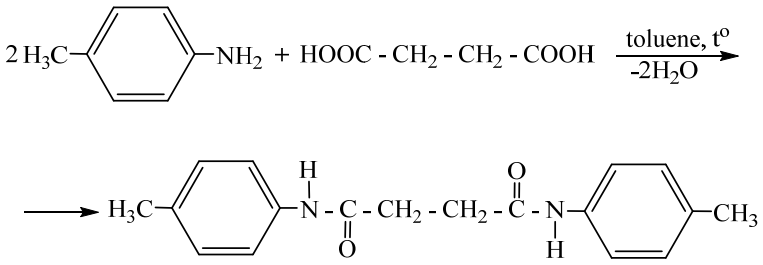


Fig. 8. Hydrogen bonds in the molecule of mono-(4-methylphenylammonium) succinate

The synthesis reactions of amide-linked compounds were carried out based on literature data [8-12], for example, with some isomers of toluidine, with oxalic acid, malonic and succinic acids, heated in toluene. The reactions carried out showed that the two carboxyl groups in the carboxylic acid molecule were completely reacted:





Scheme 4. Reactions of toluidides with carboxylic, malonic, and succinic acids

Table 2 presents alternative conditions, product yields, and physical constants for the reactions of isomeric toluidines with oxalic acid, malonic, and succinic acids to form salts and obtain amide-linked compounds.

Table 2. Alternative conditions for the reactions of toluidine isomers with oxalic, malonic and succinic acids, yields and physical constants of the compounds obtained

Name of reagents	Mole ratios of reagents	Reaction duration, hours or days	Solvent	Product yield, %	Product $t_{liquid.}$, ^0C
o-Toluidine+ *oxalic* acid	2:1	0,5 hour	Ethanol	91	183-185
o-Toluidine + malonic acid	1:1	7 day	Ethanol	87	125
o-Toluidine+succinic acid	1:1	7 day	Ethanol	88	133-135
m-Toluidine+ oxalic acid	2:1	0,5 hour	Ethanol	95	162-165
m-Toluidine + malonic acid	1:1	3 day	Ethanol	91	93-95
m-Toluidine+succinic acid	1:1	7 day	Ethanol	89	190-192
p-Toluidine+ oxalic acid	2:1	0,5 day	Ethanol	97	170-173
p-Toluidine + malonic acid	1:1	7 day	Ethanol	93	99-101
p-Toluidine+succinic acid	1:1	7 day	Ethanol	91	102-105
o-Toluidine+ oxalic acid	2:1	3 hour	Toluene	87	155-158
m-Toluidine + malonic acid	2:1	8 hour	Toluene	81	158
o-Toluidine + malonic acid	2:1	8 hour	Toluene	74	163-165
p-Toluidine+succinic acid	2:1	3 hour	Methanol	67	148-150

IR-analysis. According to IR spectrum of the salts obtained the valence of the $\equiv N^+$-H bond characteristic of the protonated nitrogen atom is observed at 2575-2944 cm^{-1}, the deformation at 1376-1386 cm^{-1}, the valence at 1514-1599 cm^{-1}, the valence at 1633-1651 cm^{-1}, the valence of the C=O bond in the amide bond, and the valence vibrations of the N-H bond in the amide bond are observed at 3164-3282 cm^{-1}, confirming the formation of an amide bond. The observation of the disappearance of the carboxyl group and free amino group vibrations in the IR spectra of the resulting compounds compared to the IR spectra of the initial aromatic amines and carboxylic acids used in the reaction (Figures 1 and 2) indicates that the reactions formed a salt at room temperature, and the reactions carried out in toluene, which removes water from the reaction mixture by forming an azeotropic mixture, formed amide-linked compounds [13-19].

Table 3. Results of IR spectra of salt and amide-linked compounds obtained as a result of the reactions of toluidine isomers with oxalic, malonic and succinic acids, cm^{-1}

The name of substances	N^+-H (v)	COO^- (v)	Valence vibrations of the	Deformational vibrations of the	Stretching vibrations of the C-N

			C=C bond in an aromatic ring	substituted benzene ring	bond of carbon in an aromatic ring
Di-(2-methylphenyl-ammonium)oxalate	2575 2865	1587 sim.	1503	739-762	1297
Di-(3-methylphenyl-ammonium)oxalate	2647, 2928	1599-1622 sim.	1492	687, 709, 742	1225
Di-(4-methylphenyl-ammonium)oxalate	2645, 2924	1558-1595 sim.	1517	762	1296
Mono-(2-methylphenylammonium) malonate	2678, 2935	1552 sim.	1418	696	1248
Mono-(3-methylphenylammonium) malonate	2582, 2924	1375 δ; 1558 sim.	1492	782	1264
Mono-(4-methylphenylammonium) malonate	2594, 2963	1386 δ; 1570 sim.	1516	784-804	1261
Mono-(3-methylphenyl-ammonium) succinate	2629, 2944	1534 sim.	1493	777	1289
Mono-(4-methylphenylammonium)succinate	2620, 2929	1514	1413	802	1286
Di-(2-methylphenyl)amide of oxalic acid	3164 (NH)	1633 (C=O)	1497	712-758	1185
Malonic acid di-(3-methylphenyl)amide	3282 (NH)	1651 (C=O)	1402-1453	744-819	1263
Malonic acid di-(2-methylphenyl)amide	3290 (NH)	1662 (C=O)	1401-1454	752-820	1263
Di-(4-methyl-phenyl)amide of succinic acid	3397 (NH)	1704 (C=O)	1392	714	1290

In the ^{1}H NMR spectrum of the synthesized quaternary ammonium toluidinium salts and toluides, the signals of the exchanged aromatic ring, the methyl group in the toluidine molecule, the methylene group in the carboxylic acid molecule, and the protons in the amide bond were observed (Table 4).

Table 4. Results of ^{1}H NMR spectra of salt and amide-linked compounds obtained as a result of the reactions of toluidine isomers with oxalic, malonic and succinic acids

	CH_3	Disubstituted aromatic ring protons	CH_2	NH
Mono-(4-methylphenyl-ammonium)malonate	2,02-2,2, singlet	6,37-6,41, dublet (C_6H_4-3,5); 6,71-6,78, dublet (C_6H_4-2,4)	4,1-4,25, singlet	
Mono-(2-methylphenylammonium) malonate	2 , singlet	6,37-6,45 , triplet - dublet (C_6H_4-4); 6,47-6,53 , dublet (C_6H_4-3); 6,75-6,82 м.у. мультиплет (C_6H_4-2,4)	5 , singlet	

Mono-(4-methylphenyl-ammonium) succinate	2,04-2,18, singlet	6,36-6,43 , dublet (C_6H_4-3,5); 6,72-6,77 dublet (C_6H_4-2,5)	4,5 , singlet	
Di-(2-methylphenyl)amide of oxalic acid	2,04-2,09, singlet	6,38-6,47 triplet (C_6H_4-5); 6,48-6,52 dublet (C_6H_4-3); 6,69-6,82 multiplet (C_6H_4-4,6)		4,36-4,48 , singlet
Malonic acid di-(3-methylphenyl)amide	1.97-2.04 singlet	6,90-6,95 va 7,32-7,37 dublet		9,48-9,5, singlet

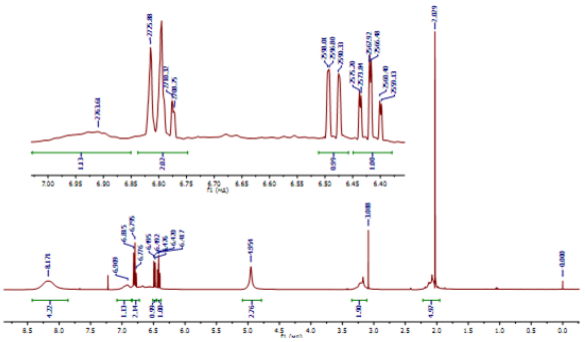


Fig. 9. ^{1}H NMR-spectrum of mono-(2-methylphenylammonium) malonate

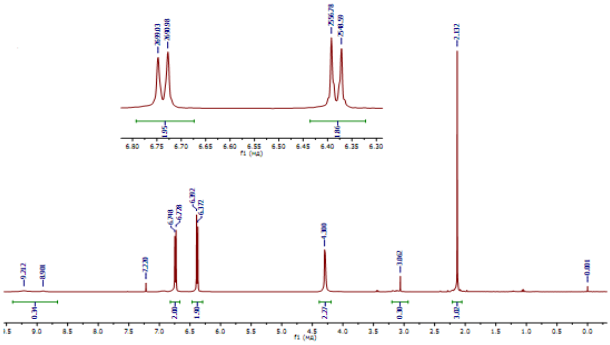


Fig. 10. ^{1}H NMR-spectrum of mono-(4-methylphenylammonium) malonate

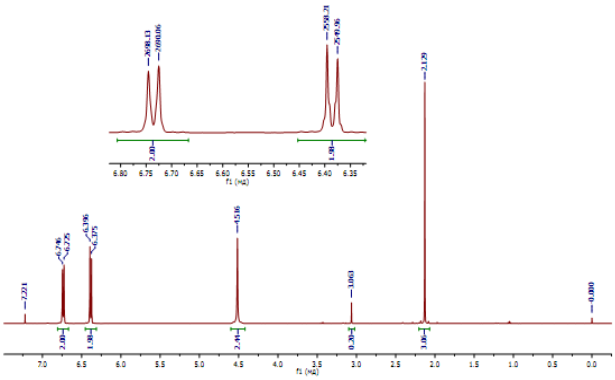


Fig. 11. ^{1}H NMR-spectrum of mono-(4-methylphenylammonium) succinate

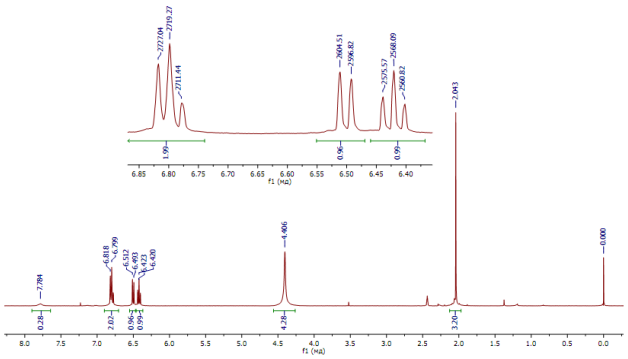


Fig. 12. ^{1}H NMR-spectrum of di-(2-methylphenyl) amide of oxalic acid

Conclusion

As a result of the research, it can be said that the reactions of toluidine isomers with oxalic acid, malonic, and succinic acids at room temperature gave salts, and when heated, amide-linked compounds were obtained. The structure of these obtained compounds was analyzed using IR spectra:

i. in the IR spectrum of the toluidine salts obtained as a result of the study the valence band of the $\equiv N^+$-H bond, characteristic of the nitrogen atom to which the proton is attached, is 2575-2944 cm^{-1}, the deformation band at 1376-1386 cm^{-1}, characteristic of the carboxyl anion that has given up its proton, and the valence band at 1514-1599 cm^{-1}.

ii. in the IR spectrum of the corresponding amide-bonded compounds, the valence vibrations of the C=O bond in the amide bond at 1633-1651 cm^{-1} and the valence vibrations of the N-H bond in the amide bond at 3164-3282 cm^{-1} were observed, confirming the formation of an amide bond, which confirms the formation of the resulting substances.
iii. According to the results of the research, new quaternary ammonium salts were synthesized, as well as new organic compounds that can exhibit high biological activity and can be used as research objects for further studies.

Conflict of Interest

The authors declare no conflict of interest.

Authors' Contribution Statement.

Akhmedov U: data curation and formal analysis, investigation, methodology, and original draft. Abdushukurov A.K: review and editing.conceptualization. Tajimukhamedov H.S and Ashurov J.M: writing (original draft), and supervision. All authors have read and agreed to the published version of the manuscript.

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