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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

THE ROLE OF NON-COVALENT INTERACTIONS IN THE SYNHESIS AND DESIGN OF 1,1-DİCHLORODİAZADİENES

Specialty: 2306.01 – Organic chemistry
Field of science: Chemistry
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INTRODUCTION

Actuality and analizing the subject. Although aromatic nitro compounds don't widely exist in nature, using their synthetic analogues in industry, medicine and other important fields make them significantly useful in organic synthesis. The reason of these syntheses is the application of various functional derivatives of aromatic nitro compounds as dyes, explosives, high energetic compounds, antimicrobial drugs and so on. Despite the fact, that nitro compounds demonstrate some negative effect on the human body, above mentioned properties underline their application importance. From this point of view, the synthesis of 1.1-dichlorodiazadienes derivatives on the basis of o, m, and p-nitrobenzaldehyde at catalytic olefination conditions is an actual direction. The actuality of this work is underlined by X-Ray method investigation of inter and intramolecular noncovalent bonds (halogen, pnicogene) between nitrogen and oxygen-based on electron-withdrawing properties of the nitro group and the effect of the position of the nitro group in an aromatic ring on crystal design and antimicrobial activity of compounds. In addition to this, the investigation of the effect of electron-donating and electron-withdrawing groups in hydrazine fragment on the reaction direction and explanation of the regularity of formation of new reaction products pharmazanes is an important point from the position of fine organic synthesis. It must be mentioned the investigation of intermolecular interaction by the modern method Hirshfield surface analysis and comparative analysis of the antimicrobial activity of 1.1-dichlorodiazadienes on the basis of hydrazine fragments with nitro groups where methyl and dimethyl groups were introduced.

In solvolysis of 1,1-dichorodiazadiens in a presence of alcohol, hydrozo derivatives of phenylacetic acid esters are synthesized, which are useful synthons in organic synthesis. The presence of the azo group in the structure of 1.1-dichlorodiazadienes and application of them as azodyes ones more increases the actuality of PhD thesis. The presence of intramolecular pnicogen bonds and intermolecular hydrogen and halogen bonds, as well as $\pi \cdots \pi$ bond interaction and their role in stabilisation of structures of azodyes, the formation of E-isomers and for the first time the investigation of the effect of these bonds on adsorption properties of these compounds, add specific brightness to the actuality of the work.

Purpose and object of research. The object of research is 1,1-dichorodiazadiens, the purpose of research is investigation of non-covalent bonding in synthesis of dichlorodiazadiens, as dyes and their antimicrobial properties.

The goal and position of the investigation. The main goal of the work is the synthesis of 1.1-dichlorodiazadienes derivatives on the basis of o, m, p-nitrobenzaldehyde at catalytic olefination conditions, the study of the role of non-covalent interaction on the formation of single crystals by X-Ray method, determination of intermolecular interaction by Hirshfield surface analysis, investigation of dye properties, antimicrobial activity of synthesized compounds and application of dichlorodiazadienes as advantageous syntones in organic synthesis.

For this purpose, those have done:

- Synthesis of polyfunctional 1,1-dichlorodiazadiene derivatives
- Study of the role of non-covalent interactions (N···Cl, Cl···O, π···π, and weak F···π halogen, CH···F-type hydrogen bonds) in the formation of single crystals based on X-Ray method, and Hirschfeld determination of intermolecular interactions by surface analysis method;
- Study of antimicrobial properties of synthesized compounds as dyes and physiologically active compounds;
- Synthesis of E / Z isomers of aryl-hydrozo derivatives of phenyl acetic acid esters from the solvolysis reaction of dichlorodiazadiene with alcohols.

Investigation methods. Synthesizing processes occurred in fine organic synthesis ETL with known methods. X-Ray Structural Analysis of these compounds was carried out using of Bruker APEX II CCD diffractometer. The NMR ^{1}H and ^{13}C spectra were obtained by the Bruker Advance 300 MHz spectrometer in solvents $CDCl_3$ and DMSO. TLC was carried out on the Silufol on UB-254, for visualization of the spots was used the KMnO4 solution and UB lamp. Column chromatography was carried out using silicagel (Merck 63-200). Mass spectrum was obtained by (ESI-MS) spectrophotometry. Elemental analysis was carried out using of Carlo Erba analysator. The antimicrobial properties of the compounds were studied at Baku State University, Department of Molecular Biology and Biotechnology, and the Ministry of Health of the Republic of Azerbaijan, the Republican Sanitary Quarantine Inspectorate.

Main provisions of thesis defense:

- Synthesis of corresponding hydrazones from o-, m- and p-nitrobenzoyaldehydes with different phenylhydrazines and synthesis of 1,1-dichlorodiazadiene derivatives in KOR presence.
- According to position of nitro group, investigation of the role of non-covalent interactions in crystal packing with X-Ray Structural Analysis, also intermolecular interactions with Hirshfeld Surface Analysis.
- Impact of nature and position of functional groups on direction of reaction and crystal packing.
- Antimicrobial properties of synthesized dichlorodiazadienes based on o-, m-, p-nitrobenzoyaldehyde.
- Study of 1,1-dichlorodiazadiens as useful synthons in organic sythesis.

The novelty of the work. For the first time, 1.1-dichlorodiazadiene derivatives were synthesized on the basis of different phenylhydrazones of o, m, p-nitrobenzaldehyde at catalytic olefination reaction conditions in the presence of catalyst CuCl, the stereochemistry of reactions was investigated by NMR and X-Ray method and it was determined that all reactions proceed with the formation of E-isomer.

X-ray method analysis allows determining the presence of inter and intramolecular noncovalent pnicogen, halogen and so on interactions in the structures of 1.1-dichlorodiazadiene. In addition to this, it was determined the effect of the nature of functional groups and functional group position in the benzene ring on crystal design.

It was determined that in comparison with other phenylhydrazones, in case of reaction proceeded with (E)-4-(2-(4(dimethylamine)benzylidene)hyd-razinily)benzonytrile, the reaction product is not subsequent 1.1-dichlorodia-zadiene, but the farmazane derivative obtained by the dimerization of phenylhydrazone.

The application of (E)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(para-substituted phenyl)-diazine which was obtained on the basis of 2-nitrobenzaldehyde as azodyes were studied. The reason of the prevailing of E-isomers is caused by the presence of intramolecular pnicogen, hydrogen and intermolecular halogen bonds.

During the investigation of antimicrobial properties of dichlorodiazadienes containing nitro, methyl, dimethyl groups, it was determined that these compounds demonstrate more effective activity against *Acenitobacter baumanii* BDU32, *Escherichia coli* BDU12, *Klebsiella pneumoniae* BDU44, *Pseudomonas aeruginosa* BDU49, *Staphylococcus aureus* BDU23 bacteria.

The hydrolysis of the alcohol solution of synthesized 1.1-dichlorodiazadienes allows obtaining the mixture of E/Z-isomers of an appropriate ester of 2-hydrozo-phenylacetic acid and as a third product 1,2-diazete.

Theoretical and practical importance of the research. Synthesized 1,1-dichlorodiazadiens have phormocor functional groups (methyl, halogen, nitro, dimethylamine), thus, they can be applied to *Acenitobacter baumanii* BDU32, *Escherichia coli* BDU12, *Klebsiella pneumoniae* BDU44, *Pseudomonas aeruginosa* BDU49, *Staphylococcus aureus* BDU23 bacterias. Furthermore (E)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(para substituted phenyl) diazines can be used as azodyes. Also these can be useful synthons in fine organic synthesis to obtain some compounds, especially ethers and 1,2-diazetes. Dichlorodiazadienes theoretically can be useful compounds in researches about new properties of non-covalent interactions (N···Cl (pinacogen), Cl···Cl (halogen), Cl···O (chalcogen), π···π, and weak F···π halogen, CH···F hydrogen bonding).

Approbation and publication of the work. Individual scientific reports and some results of the dissertation were presented and discussed at different local and international conferences.

–The Fourth International Scientific Conference «Advances in Synthesis and Complexing» RUDN University (Moscow, 2017);

–Actual problems of chemistry - XII Republic scientific conference (Bakı, 2018);

–The 2nd Struchkov Meeting, International Workshopon Chemical Crystallographyand Structural Biology, RUDN University (Moscow, 2018);

–Actual problems of chemistry – XIII Republic scientific conference (Bakı, 2019),

–The Fifth International Scientific Conference «Advances in Synthesis and Complexing» (Moscow, 2019);

–International chemical congress, Istanbul, Yildiz Technical University (İstanbul, 2019).

The main provisions of the dissertation and the results obtained were published in 21 scientific works, including 9 articles and 12 theses.

The total volume of the dissertation with a sign, indicating the volume of the structural units of the dissertation separately. The dissertation consists of an Introduction, 3 chapters, a conclusion and a list of references, covering 194 pages in A4 format. The main part of the work (excluding figures, tables, graphs and bibliography) is the sign 165479 (including Introduction – 9457, Chapter I – 47485, Chapter II – 55300, Chapter III – 51717, Conclusion – 1520). The list of used literature includes 261 sources cited in the dissertation. The dissertation contains 20 tables and 64 figures reflecting the results.

The volume of the dissertation and structure: Dissertation organized of introduction, literature review, discussion of the results, experimental part, conclusion, references and extra part and consist of 193 computer pages. The results of performed research were given in 64 figures and 20 tables. References consist of 261 citations.

Personal addition of author. Performing of the dissertation work, contender took part in debate: recent years in this field references have collected, synthesized, NMR spectrum of components have explained, ideas and results have collected and articles have written. Thus, contender either worked with organic chemists or physician-scientists, plus biologists to investigate antimicrobial properties.

The actuality of the work was justified, the purpose of the work, scientific novelty, practical importance of the work and important defending parts were described in the **introduction part.**

The first chapter dedicated to the analysis of literature review.

In the represented dissertation work, dichlorodiazadienes have synthesized in a presence of catalytic olefination reaction from benzoy aldehyde derivatives, so in a review some interesting transformations from benzoy aldehyde, N-substituted and N-non substituted hydrazone transformations in catalytic olefination reactions and recent scientific researches in this field are represented. During the researches, phrmasan derivative was synthesized, that's why in a review there are information about synthesis of pharmasans and their biological activity.

In crystal packing of synthesized compounds non-covalent interactions have found, so in a review there are information about these bondings (coordination, halogen, hydrogen, nitrogen- halogen, halogen-chalcogen, halogen-halogen, Cl···Cl, Cl···O, pinacogen N···Cl interactions etc.).

In the dissertation work, synthesis processes are based on nitrobenzoy aldehyde and their antimicrobial properties are studied, so in a review there are information about biological activity of aromatic nitro compounds.

The synthesis of 1.1-dichlorodiazadiene derivatives on the basis of o, m and p-nitrobenzaldehyde, the study of the role of non-covalent interactions (N···CI, CI···O, π···π, and weak F···π halogen, CH···F type of hydrogen bonds) in the formation of monocrystals, the determination of intermolecular interactions by Hirshfield surface analysis method, the study of dye properties of synthesized compounds as well as antimicrobial properties of physiologically active compounds and the analysis of the application of dichlorodiazadienes as advantageous sintones in organic synthesis were given in the **second chapter**.

Practical part of the research, also physical-chemical properties of synthesized compounds (^{1}H NMR, ^{13}C NMR, mess spectroscopy, Infrared spectroscopy) are shown in **the third chapter**.

MAIN CONTENT OF THE WORK

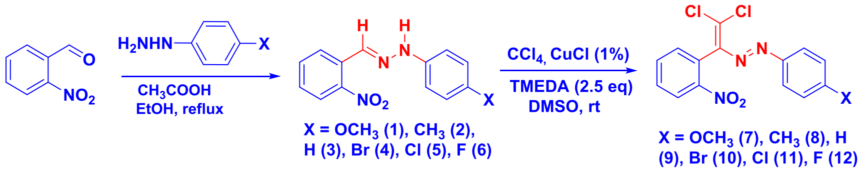
Synthesis and reactions based on polyfunctional compounds takes organic chemists' attention. That is why, synthesis and transformations of polyfunctional 1,1-dichlorodiazadienes are important, especially their solvolysis reaction with alcohol, which results with synthesis of E/Z isomers of aryl-hydro derivatives of phenylasetat esters.

In recent years, extensive research has been published on the important role of non-covalent bonds in organic synthesis, catalysis, synthesis of metal complexes, numerous monographs in this field, special issues of some high-impact journals. This allows us to say the formation of a new scientific direction in the field of chemistry. It should be noted that X-ray method is at the heart of all this. This is because the existence of non-covalent bonds in the reaction products obtained is determined only by studying the molecular structures of monocrystals. It should be noted that in some studies, work has already begun to study these relationships in solutions. It is important to note the use of NMR studies. It would be wrong to compare the strength of these ties with each other. Because in some cases there are many examples of the simultaneous effect of more than one relationship. A comprehensive study of these relationships in synthesized dichlorodiazadiene is distinguished by its relevance.

1. Synthesis of 1,1-dichlorodiazadienes from nitrobenzoy aldehydes

1,1-dichlorodiazadiene derivatives are synthesized from the reaction of proper hydrazones of some para-substituted phenylhydrazines of o-, m- and p-nitrobenzoy aldehydes, and then CuCl catalytic reaction of the last with CCl4 in a presence of KOR.

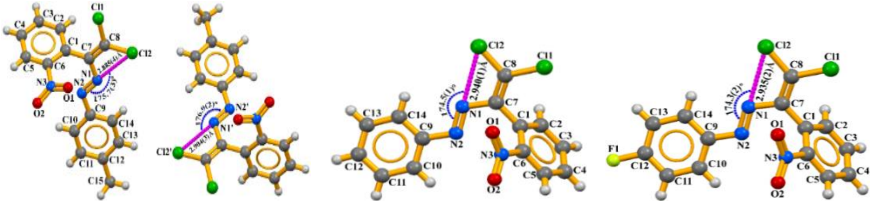
1.1. The pnicogen, halogen and hydrogen bonds in (E)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(para-substitutedphenyl)-diazines. The series of (E)1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(para-substituted phenyl)diazine were synthesized on the basis of o-nitrobenzaldehyde and from the point of intermolecular pnicogen bond structure-properties interaction, as well as the strength of intermolecular hydrogen bond were systematically investigated (scheme 1). Para-substitutors in aromatic ring consist of electron-donating ($-OCH_3$ and $-CH_3$) and electron-withdrawing (−Br, −Cl and −F) groups.



Scheme 1. The synthesis of compounds **1–12**

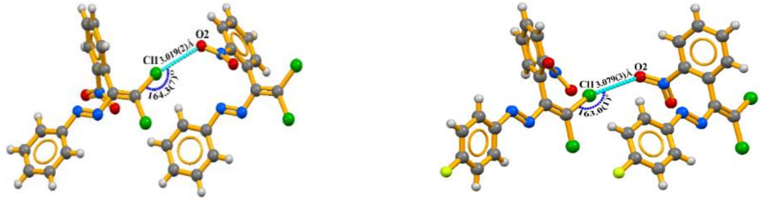
X-Ray Structural Analysis of **8**, **9** and **12** monocrystalls show that, these molecules which have strong intramolecular pnicogen bondings, in 1-4 membered rings N=N···Cl in proper angles N···Cl intereactions are 175.7 (3)° , 2.885 (4) , 176.9 (2)° , 2.904 (3) Å (**8**), 174.5 (1)° , 2.940 (1) Å (**9**), 174.3 (2) ° , 2.935 (2) (**12**) , that are smaller than accepted Van der Vaals radius (N + Cl=1.55 +

1.75=3.30 Å) (figure 1). In crystal packing of 8, we can see two detached molecules with Cl···O halogen bonding (3.019 (2) və 3.079 Å) which have different intramolecular pnicogen bondings. Also C−Cl···O halogen-chalcogen non-covalent bondings with 164.3 (7) və 163.03° angles in **9** and **12** are smaller than accepted Van der Vaals radius (Cl + O=1.75 + 1.52=3.27 Å) (figure 2). In 12, F (1) atom behaves as halogen bonding donor and acceptor with H-interaction directs to the close aromatic π system, and CH fragment of aromatic part weaks the weak intermolucular F···π halogen bonding, and CH···F hydrogen bonding (3.754 və 2.699Å) (figure 2). All structures are stabilizated with many weak intermolecular hydrogen bondings, also with π···π interactions.



8 **9** **12**

Figure 1. The crystal structure of **8, 9** and **12** considering relative numbering of atoms**.**



9 **12**

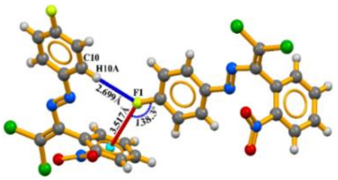


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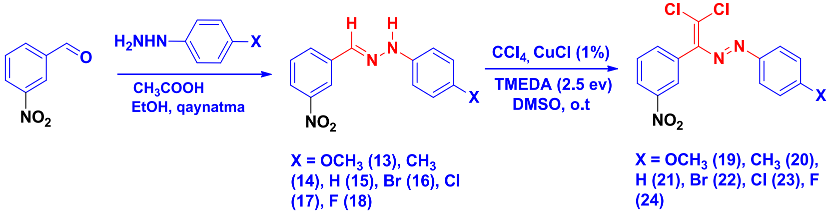
Figure 2. Intermolecular halogen bonds of **9** and **12** (was demonstrated by broken green and blue lines)

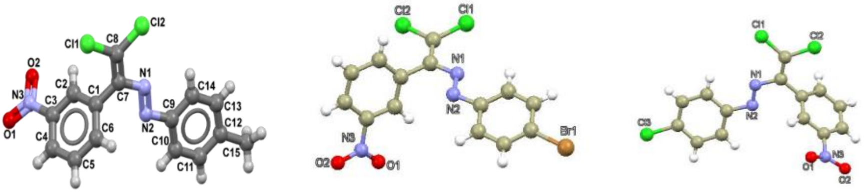
As a result, it was determined the total role of non-covalent bonds (intramolecular pnicogen and intermolecular hydrogen and halogen bonds, as well as π···π interaction) in the formation of dichlorodiazadienes monocrystals. In addition to this, the application of the last ones as diazo dyes was investigated and positive results were obtained.

1.2 X-Ray Analysis and synthesis of dichlorodiazadienes from m- and p-nitro benzoy aldehyde. According to NMR, RSA an UV results of corresponding dichlorodiazadienes which were sintesized from o-nitro benzoy aldehyde, researches about reactions of m- and p-benzoy aldehyde are proceeded. Our purpose to pursue this is to investigate the state of nitro group in benzol ring and its influence on crystal packing, yield and direction of a reaction. First, corresponding phenylhydrazones of m-nitro benzoy aldehyde have been synthesized, then analogously dichlorodiazadienes have synthesized from the last.



Scheme 2. Synthesis of **13-24** compounds

Structures of substances were investigated by NMR, Mass Spectroscopy and X-Ray Structural Analysis (figure 3).

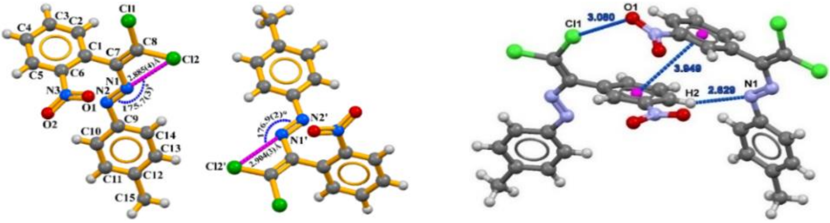


20 **22** **23**

Figure 3. The structures of **20, 22** and **23**

As we noted before, main purpose of these reactions is investigating the influence of nitro group on crystal packing. The only difference in these compounds is the state of nitro group in the aromatic ring. Similarities and differences of molecular designing of the compounds **8** and **20** can be seen in images below.

Intermolecular π···π interactions were observed between benzene rings during looking at crustal structures. But these interactions in case of compound **8** were between benzene fragments of aldehyde and hydrazine [4.022 Å], whereas in case of compound **20** were observed just between benzene fragments of aldehyde [3.948 Å].



8 **20**

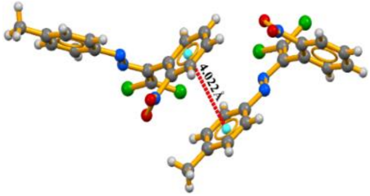


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Figure 4. Comparative investigation of **8** and **20** compounds

In the case of compound **20** were observed just intermolecular Cl···O halogen bonds [3.080Å], whereas in the case of compound **8** the presence of intermolecular Cl···N [2.885Å and 2.905Å] pnicogen bonds were determined. In addition to this, unlike compound **8**, in the case of compound **20** weak H···N hydrogen bond [2.829Å] was observed. As a result of these comparisons, it is possible to conclude that changing of position of the functional group will allow the controlling of crystal design.

The comparison of crystal structures of compounds **22** and **23** bearing Cl and Br atoms in hydrazine fragment will allow saying that their crystal design is close to each other. Thus, intermolecular Cl···π and O···Cl and intramolecular Cl···N interactions were observed in both molecules.

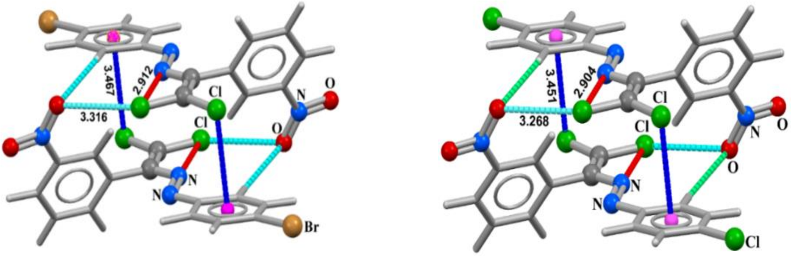
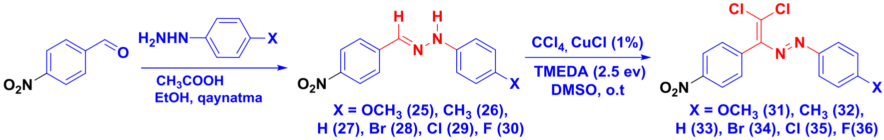


Figure 5. Comparable investigation of compounds **22** and **23**

As it can be seen from the molecular structure, due to the fact that the molecules stand in front of each other by the head-foot principe, the halogen atoms (Br, Cl) in the hydrazine fragment do not take part in any interactions. Cl atoms in the vinyl group with hydrazine fragment benzene ring take part in the formation of interactions such as intermolecular double bonds ···π, intramolecular Cl···N and intermolecular Cl···O non-covalent bonds, which result in the location of molecules by head-foot principe during the formation of crystal cell.

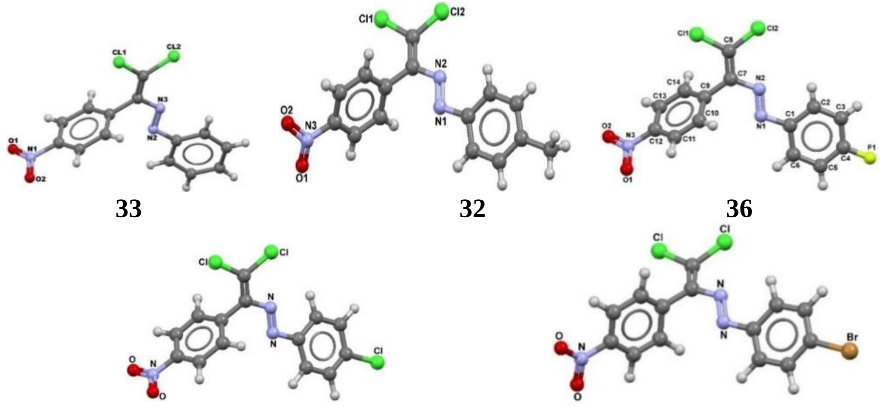
So, we can explain that, crystal designing of **22** and **23** and totally polyfunctional compounds is related to complete interactions of different non-covalent bondings. So it is not right to take any of these non-covalent bonding as a primary.

Considering all the above mentioned, hydrazones of p-nitrobenzaldehyde with subsequent phenylhydrazines and dichlorodiazadienes under catalytic olefination conditions in the presence of the catalytic amount of CuCl were synthesized.



Scheme 3. The synthesis of compounds **25-36**

The structures of synthesized compounds were investigated by NMR and X-ray single-crystal method.



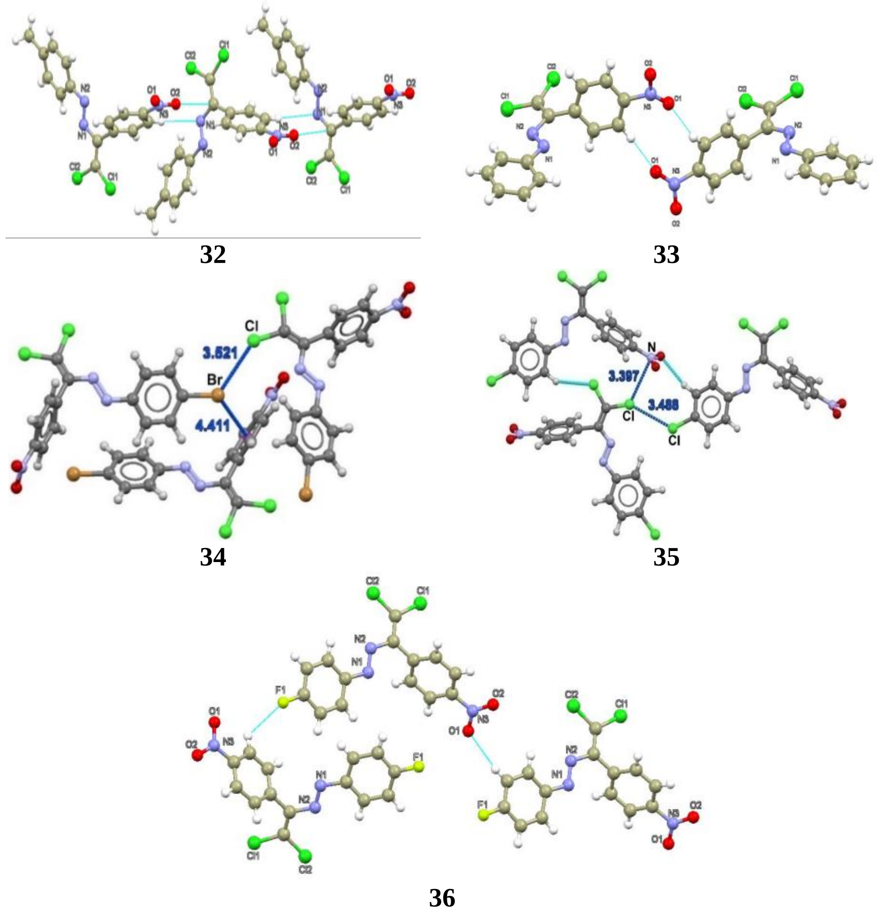
33 **32** **36**

35 **34**

Figure 6. Molecular structures of **32-36**.

X-Ray Analysis of **32-36** compounds let us to know non-covalent bondings (halogen, pinacogen, hiydrogen, halogen-π) in crystal packing.

Due to the presence of halogen atoms in para position at hydrazine fragment, noncovalent interaction between this halogen atom at the para position and chlorine atom at the vinyl group –Cl···Cl [3.488Å], Br···Cl [3.521Å] play a role in the formation of the crystal. In **34** Br···π [4.411 Å] interaction was found. But in para position only intermolecular hydrogen bonding has a main role in crytal packing if CH_3 **(32)**, F(**36**), and H(**33**) (figure 7).



32 **33**

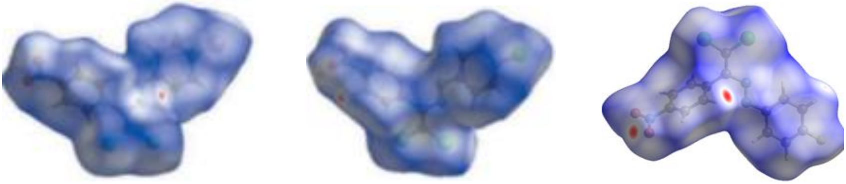
34 **35**

36

Figure 7. Inter and intramolecular bonds of compounds **32-36** were given by broken lines.

In contrast to the dichlorodiazadienes (**36**), in p-benzoy aldehyde case (**34** and **35**) non-covalent interactions (Br···Cl, Cl···Cl) between Cl atoms and vinyl group of para-positioned halogen atoms were observed and their main role in crystal designing was found. In contrast to the halogen atoms, it shows the effect of the state of nitro group in benzol ring on crystal packing. In meta position, halogen atoms of crystal in vinyl group take part in different non-covalent (Cl···π, N···Cl, Cl···O) interactions and make the crystal form as a head-to-tail principle. Also effect of nature of p-positioned halogen atoms on crystal designing was found. Thus, unlike bromine and chlorine atoms, in case of fluorine atoms, noncovalent intermolecular bonds were not determined which is caused by the fact that fluorine atom weakly participates in such type of interaction.

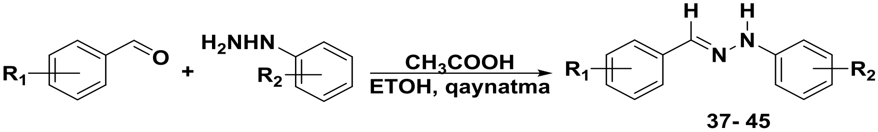
In recent years, crystal structures of three isotop compounds, (E)-1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)vinyl]diazine **34**, (E)-1-(4-chlorphenyl)-2-[2,2-dichloro-1-(4-nitrophenyl) etenyl]-diazine **35** and (E)-1-(4-fluorphenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)etenyl]diazine **36** were used in Hirshfeld Surface Analysis to investigate intermolecular interactions.



34 **35** **36**

Figure 8. Compounds **34-36** Three-dimensional Hirshfeld Surface

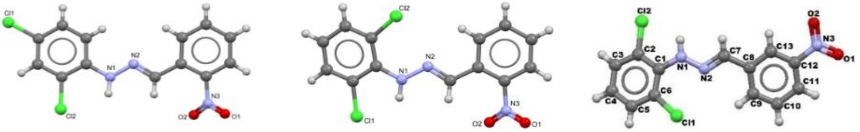
1.3. X-Ray Structural Analysis and synthesis of corresponding dichlorodiazadienes from 2,4-; 2,6-; 3,4-dichlorophenylhydrazones of o-, m- and p-nitrobenzaldehydes. Dichlorodiazadienes (**10, 22, 23, 34, 35, 36**) which were synthesized from o, m, p-nitrobenzaldehyde and keep para positioned halogen atoms in hydrazine fragment, have an impact on crystal designing. So, according to this, our studies about 2,4-; 2,6-; 3,4-dichlorophenylhydrazines are pursued (scheme 4). Main purpose is to understand the impact of Cl atoms of synthesized compounds in hydrazine fragment, also state and the quantity.



R_1=o, m, p-NO_2-, R_2= 2,4-dichloro-, 2,6-dichloro-, 3,4-dichloro-.

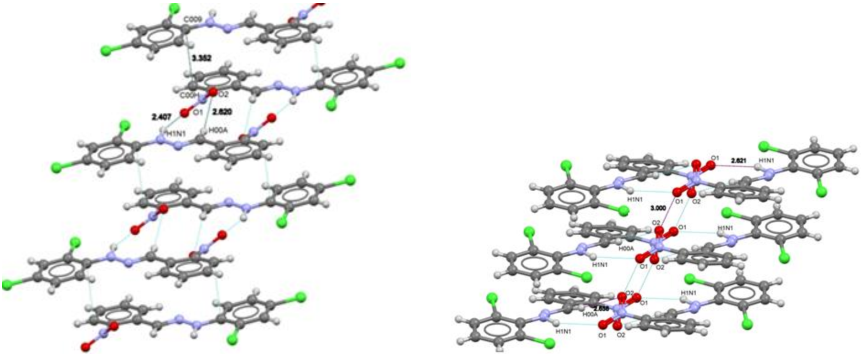
Scheme 4. The general scheme of Schiff type hydrazones 37-44 synthesis

Along with the synthesis of dichlorodiazadienes on the basis of phenylhydrazones, the X-ray single-crystal method investigations were performed for the investigation of the effect of functional groups in the benzene ring on crystal design.

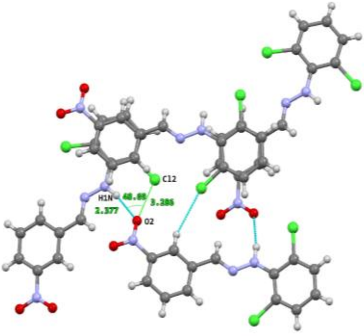


37 **38** **41**

Figure 9. The molecular structure of compounds **37, 38** and **41**



37 **38**



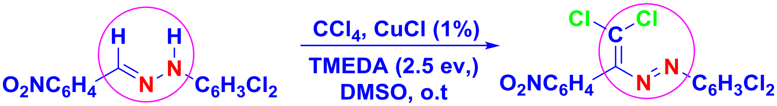
41

Figure 10. The molecular structures of 1-(2,4-dichlorophenyl)-2-(2-nitrobenzylydene)hydrazine **(37),** (E)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylydene)hydrazine **(38)** and (E) -1- (2,6-dichlorophenyl) -2- (from 2-nitrobenzyl) hydrazine **(41)**

As a result, depending on the position of nitro groups and chlorine atoms in the benzene ring the formation of different designs during crystal packing was observed. So, it is possible to result that the changing of position of the nitro group in benzaldehyde and chlorine atom in phenylhydrazine will lead to the new design of the crystal cell.

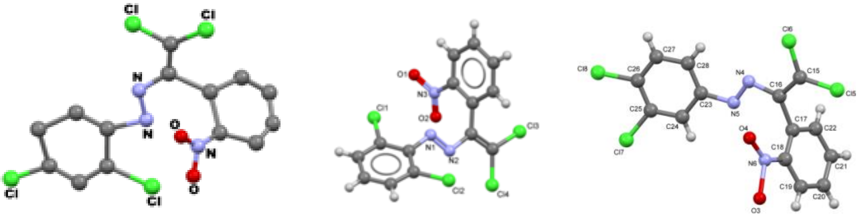
It must be mentioned that despite the presence of two chlorine atoms in the molecules of hydrazine, unlike dichlorodiazadienes, Cl···Cl interactions were observed in these molecules. This can be connected by the formation of strong intermolecular hydrogen bonds in the structure of phenylhydrazones, the maximum prolonging of the distance between Cl atoms during packing of crystals, otherwords, packing of the molecules by the head-tail principe. The role of non-covalent interactions (O···HC (2.58Å), O···NH(2.377Å), O···Cl (3.164Å), O···O(3.000Å) in the formation of crystals of phenylhydrazones were determined.

Corresponding **46-54** dichlorodiazadienes were synthesized from **37-45** phenylhydrazones (scheme 5).



Scheme 5. The total synthesis of **46-54** compounds

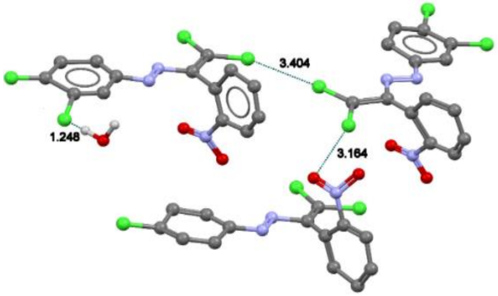
Structure of dichlorodiazadienes was proved by NMR, XRA. Molecular structures of compounds are represented in figure 11.



46 **47** **48**

Figure 11. Molecular structure of compounds

To study the effect of number of Cl atoms on crystal designing, monocrystals were formed from compounds which were synthesized by only orto nitro benzoy aldehyde, and were investigated by X-Ray Structural Analysis. We found that, in **48** halogen atoms in benzol ring do not attend in crystal packing. Main reason for this is that, Cl atom in vinyl group has non-covalent bondings with O atom of nitro group (Cl···O (3.554 Å) in other molecul and Cl atom of vinyl group (Cl···Cl (3.404Å) in other second molecul, and halogen atoms were not able to attend in crystal packing (figure 12).



41

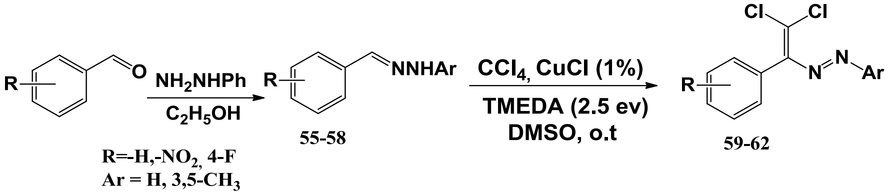
Figure 12. Intermolecular non-covalent interactions of compound **48** were demonstrated by green broken lines.

Thus, it can be concluded that there is no serious regularity in the formation of crystals. This suggests that various non-covalent bonds play a main role in polyfunctional compounds from time to time.

1.4. The effect of functional groups of phenylhydrazones on crystal design and reaction directions. Considering the effect of nature, position and quantity of aldehyde and hydrazine fragments in the structure of dichlorodiazadienes which were synthesized on the basis of o, m, p-nitrobenzaldehydes on the formation of crystal cell as well as a thorough effect on crystal design, novel research were performed in this direction. Thus, by the introduction of nitro, fluorine, dimethylamine, methoxy groups in the aldehyde fragment and electron-donating methyl (4-CH_3; 3,5-$(CH_3)_2$) and electron-withdrawing cyano (4-CN) groups in the hydrazine fragment, corresponding dichlorodiazadienes were synthesized and their X-ray single-crystal investigations were performed. It was determined that even in some cases functional groups impact on reaction direction. It is also possible to say in the beginning that these synthesized compounds will demonstrate biological activity. It makes possible to say the presence of the azo group, heminal dichloro substituted double bond, pharmacophoric CH_3 and NO_2 groups in the structure of compounds.

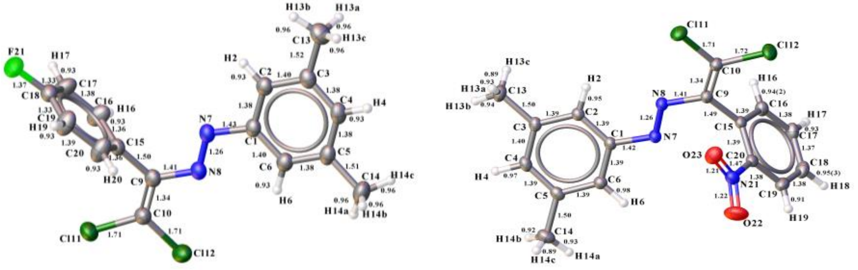
First of all, halogen atoms in hydrazine fragments were replaced by electron-donating dimethyl groups, the reactions of them with 2-

NO_2 and 4-F benzaldehydes were performed and the crystal structures of synthesized compounds were comparatively investigated with the structure of compound A which was obtained in the previous synthesis. The main goal of such choice was as well as the synthesis of dichlorodiazabutadiene derivatives and the study of new non-covalent interactions in the structure of obtained compounds. The reactions of phenylhydrazones, which was obtained on the basis of phenylhydrazine and 3.5-dimethylphenylhydrazine, with CCI_4 were investigated (scheme 6).



Scheme 6. The general scheme of synthesis of compounds **55-62**

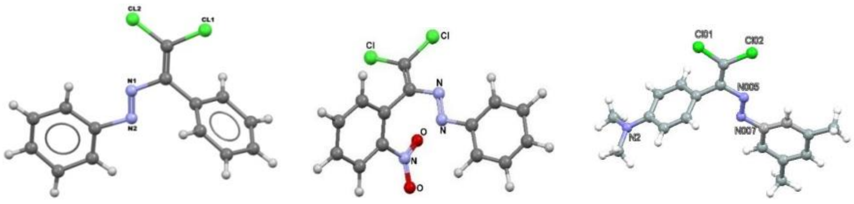
The single-crystals of synthesized compounds (**59, 61** and **62**) were obtained and their molecular structures were determined by X-ray single-crystal method (figure 13). The presence of Cl···Cl interactions and its parameters were also determined by X-ray single-crystal method.



61 **62**

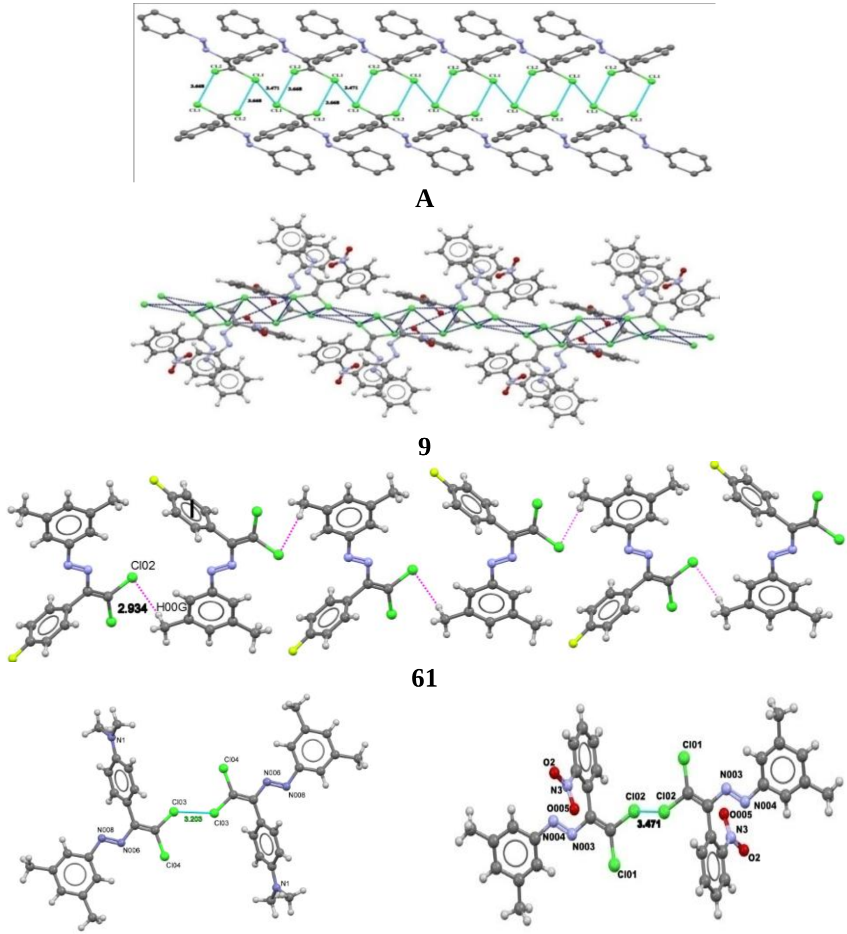
Figure 13. Molecular stuructures of compounds **61** and **62**

Crystal structures of obtained compounds (**61, 62**) were compared with **A** (E)-1-(2,2-dixlor-1-phenylvinyl)-2-phenyldiazene**, B** 4-(2,2-dichloro-1-((3,5-dimetylphenyl) diazenile) vinyl)-N,N-dimetilanilin və **9** (E)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-phenyldiazen compounds from previous researches.



A **9** **B**

Figure 14. The molecular structure of dichlorodiazaadiene derivatives



A

9

61

B **62**

Figure 15. Intermolecular non covalent Cl···Cl interactions were demonstrated by broken lines

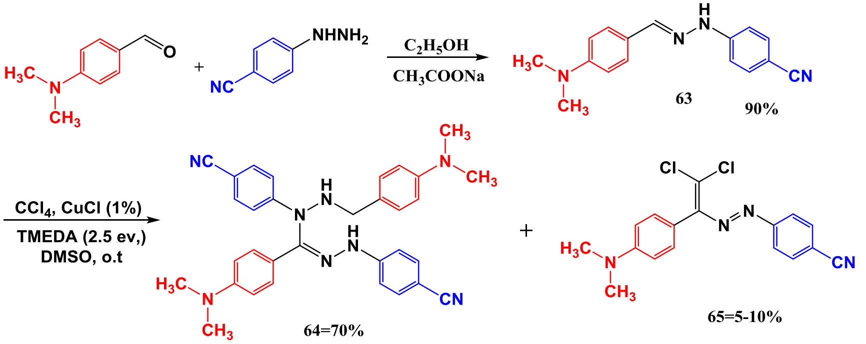
In comparison with **A** it is clear that, electrodonor methyl groups in phenylhydrazine molecul, electroacceptor nitro group and F atom in aldehyde molecul has an impact on crystal designing, capacity of the crystal, quantity of molecules and thus, parameters of intermolecular non-covalent bondings.

Unlike synthesized **9** (E)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-phenyldiazene, **B, və 62** (E)-1-(2,2-dichloro-1-(2-nitrophenyl)-vinyl)-2-(3,5-dimetilphenyl)diazene in previous researches, Cl···Cl interactions in **61** (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(3,5-dimethylphenyl) diazene were not observed. Unlike **9, A, B** and **62,** in **61** H atoms in CH_3 group make new Cl--H hydrogen bondings with Cl atoms of vinyl group in close molecul and Cl atoms place in a maximum distance from each other and do not attend in crystal designing.

It can be concluded that the nature of the functional groups in the benzene ring has a profound effect on the crystal design.

As a result, it was determined that the introduction of various functional groups in the structure of benzaldehyde and phenylhydrazine has an impact on parameters of non-covalent interactions and these interactions have a significant effect on crystal design.

The research was continued by replacing the electron-withdrawing nitro group with electron-donating dimethylamine group. In comparison with other phenylhydrazones, the main product of the performed in the same conditions reaction by using (E)-4-(2-(4(dimethylamine) benzylidene)hydrazinyl)benzonyt-rile, which was synthesized on the basis of 4-dimethylaminobenzaldehyde and 4-cyanophenylhydrazine, is not subsequent dichlorodiazadiene, but pharmazane derivative which was obtained during dimerization of phenylhydrazone (scheme 7).



Scheme 7. The general scheme of synthesis of compounds **63-65**

The reason of obtaining of pharmazane derivative is caused by the different electron density of benzene ring in the structure of (E)-4-(2-(4(dimethylamine)benzylidene)hydrazinyl)benzonytrile. As a result of π-π non-covalent interactions between benzol rings, crystal has a compact structure which allows hydrazone dimerisation. Structure of hydrazone was proved by NMR and X-Ray Structural Analysis methods and found that, in a solvent π-π non-covalent interactions between benzol rings makes distance smaller between molecules and this results with combinin hyrdazone molecules (figure 16).

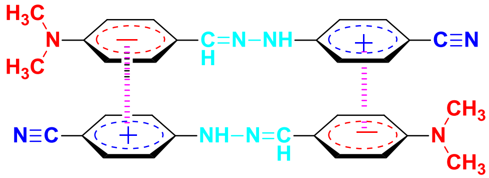
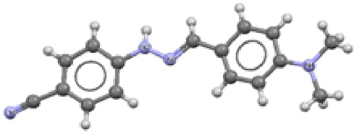
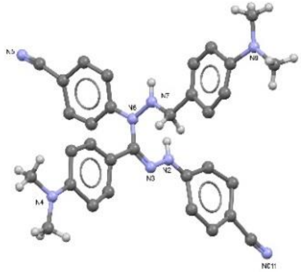


Figure 16. π-π interactions between benzene rings.

The structures of synthesized compounds **63-65** were determined by X-ray single-crystal method.



63



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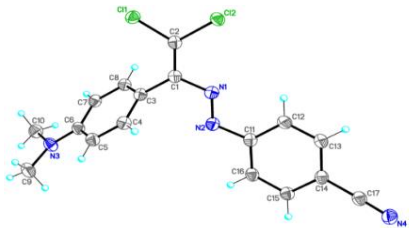


65

Figure 17. The molecular structure of obtained compounds.

Concerning these positive sides of pharmazones, this reaction can be used as a novel synthesize method of a wide spectrum of farmazanes.

As it can be seen from the molecular structure, the molecules as much as possible close in the horizontal direction by nail-nail principe and in the vertical direction by head-nail principe as a result of gravitation between benzene rings which leads to the **π-π** interactions (2.852Å) and also the presence of two hydrogen bonds (2.721Å), (2.571Å), which is formed between nitrile group and adjacent molecules. This one leads to the formation of the dimerization product of 6**4** at the end (figure 18).

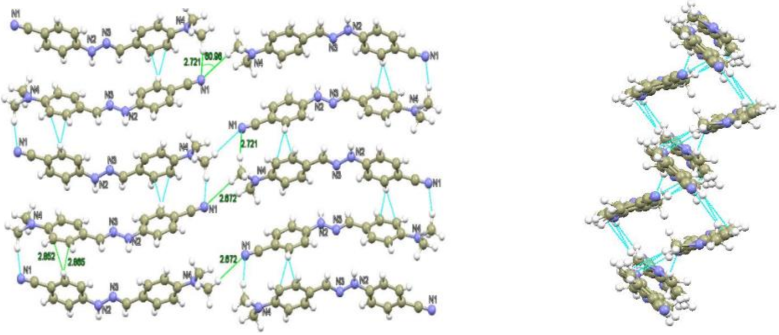
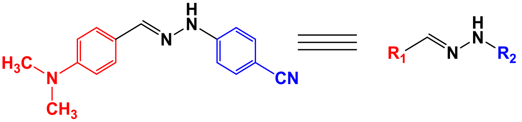
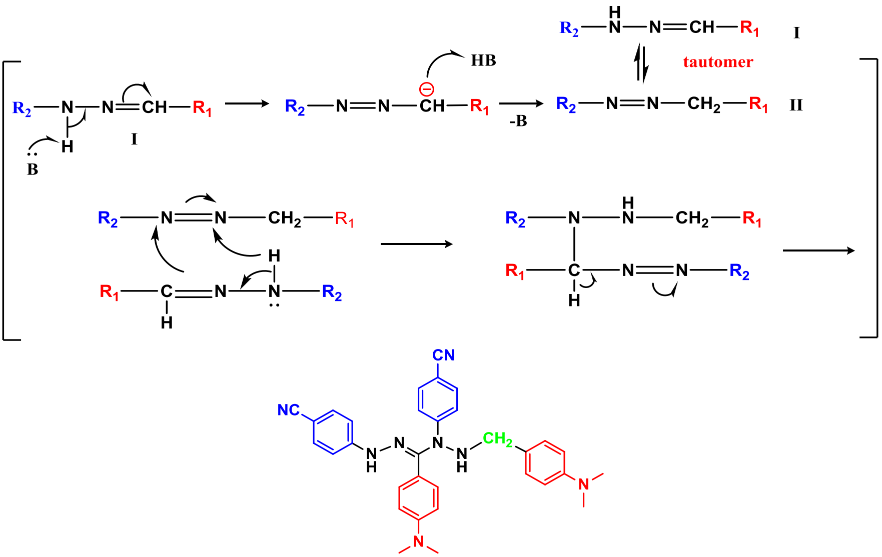


Figure 18. π-π interactions and hydrogen bond of **63** molecule were demonstrated by broken lines.

Considering above-mentioned, the probable mechanism of formation of dimerization product was demonstrated by the below-given scheme. First of all, the transformation of phenylhydrazone into its tautomer **II** has occurred in the presence of TMEDA. Afterwards, due to the close location of hydrazone molecule and intermolecular stitching (the formation of C-N bond) as well as corresponding rearrangements, the formation of pharmazane derivative of the 64 compound is occurred. In general, due to the fact that these transformations occur synchronously, the below-given scheme can be presented for the reaction mechanism.

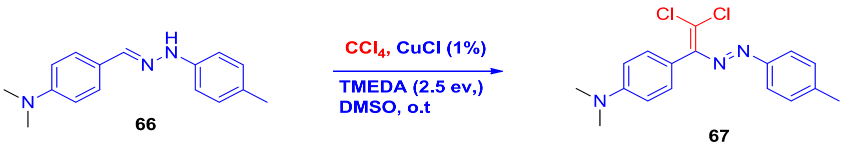




Scheme 8. The general mechanism of formation of compound 64

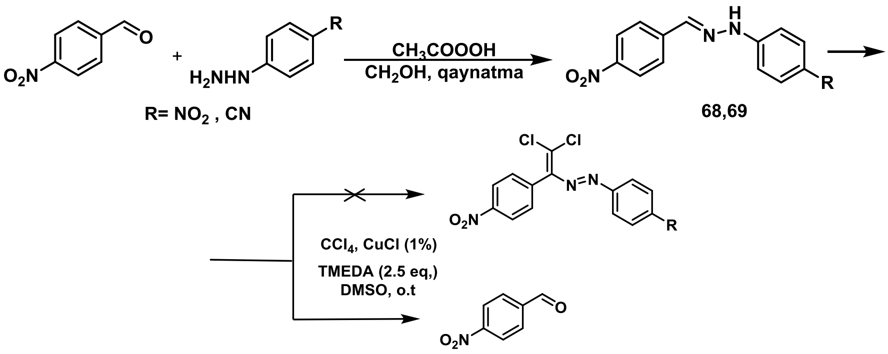
Thus, it was found that along with dichlorodiazadiene (**65**), phenylhydrazones were dimerized by attracting each other on a "head-to-tail" basis, which led to the synthesis of pharmaceuticals (**64**), the main product of the reaction.

As a continuation of research, the replacing of electron-withdrawing CN group by electron-donating CH_3 group in the hydrazine fragment leads to the formation of the only dichlorodiazadiene with high yield and the structure of compound **67** was determined by X-ray single-crystal method.



Scheme 9. The formation of (E)-4-(2,2-dichloro-1-(p-tolyldiazenil)vinyl)-N,N-dimethylaniline

By the analysis of the reaction products, it was determined that in case if both groups in the benzene ring will be electron-withdrawing groups, hydrazone is splitting on initial aldehyde and these reactions in the presence of Cu salts are unknown in the literature.



Scheme 10. The general mechanism of the synthesis performing on the basis of para-nitrobenzaldehyde

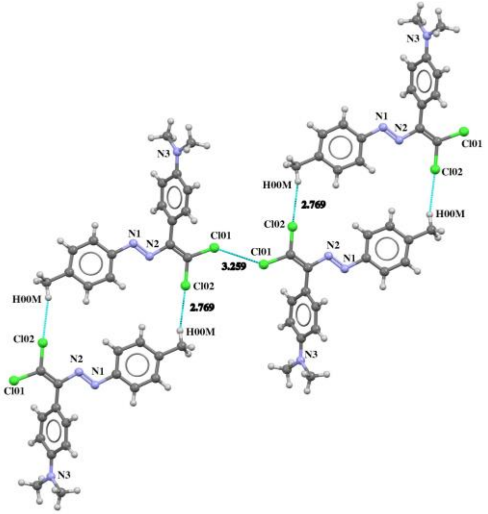
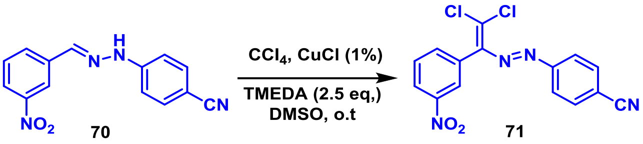


Figure 19. The molecular structure of compound **67** ((E)-4-(2,2-dichloro-1-(p-tolyldiazenil)vinyl)-N,N-dimethylaniline. The intermolecular halogen bonds in the structure of compound was given by green broken lines.

But in case if the position of the nitro group will be changed from the para position to meta position in the benzene ring, the reaction will proceed and this can be explained that m-nitro group does not participated in the delocalization.



Scheme 11. The mechanism of formation of compounds **70** and **71**

The structure of obtained compound was determined by X-Ray single-crystal method (figure 20).

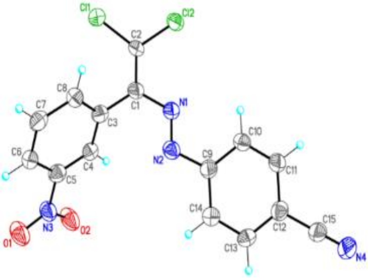
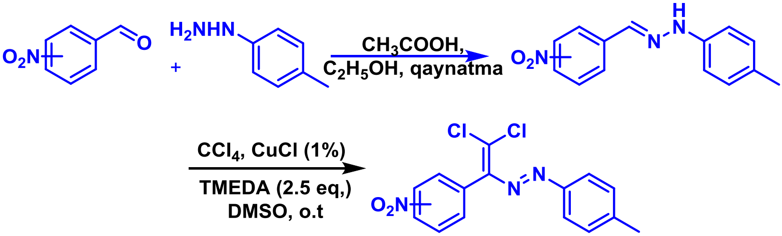


Figure 20. The molecular structure of compound **71**

Thus, based on the above reactions, it was determined that the nature and condition of the substituents in the benzene rings have a significant effect on the direction of the reaction, the yield of the products obtained, and the design of the crystal

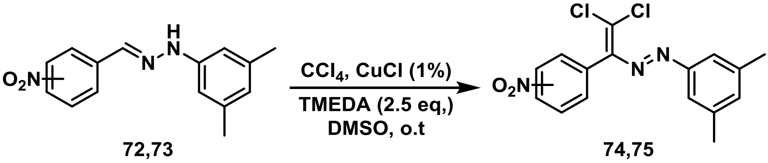
Due to the presence of azo-group, dichlorosubstituted double bond, pharmacophoric CH_3 group in the structure of synthesized compounds, corresponding dichlorodiazadienes were synthesized on the basis nitrobenzaldehydes and hydrazine fragments bearing 4-CH_3 and 3,5-$(CH_3)_2$ groups and their antimicrobial activity was investigated.

First of all, the synthesis of dichlorodiazadienes on the basis of corresponding phenylhydrazones of o, m, p-nitrobenzaldehydes and 4-methylphenylhydrazine was performed.



Scheme 12. The synthesis scheme of (E)-1-(2,2-dichloro-1-(nitrophenyl)vinyl)-2-(p-toluene)diazenes

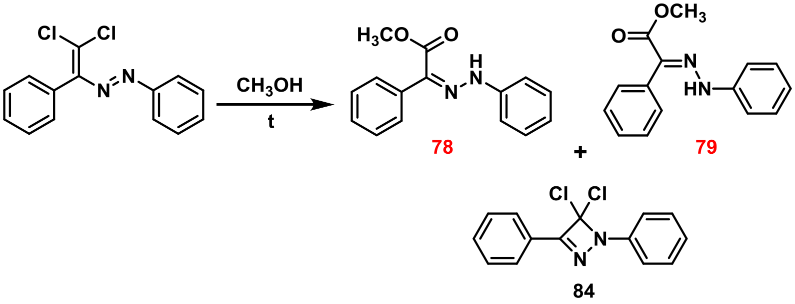
Concerning obtained results, the increasing of a number of methyl groups in the structure of synthesized compounds leading to the differences in biological activity was planned. From this point of view, leaving constant aldehydes p-toluenephenylhydrazine was replaced by 3.5-dimethylphenylhyd-razine.



Scheme 13. The synthesis scheme of (E)-1-(2,2-dichloro-1-(nitrophenyl)vinyl)-2-(3,5-dimethylphenyl)diazenes

Thus, initial antibacterial studies of these compounds demonstrate that compounds bearing 2 methyl groups is more active than the compounds with one methyl group. At the same time, considering the position of nitro groups in the aromatic ring the obtained results were significant. Thus, the activity results of dichlorodiazadienes which were synthesized on the basis of ortho-nitrobenzaldehyde were higher than in the case of para-nitrobenzaldehydes. And at the same time, looking at the crystal structure of molecules it is possible to see that the position changing of the nitro group leads to the transformations in the crystal cell design and this design, in turn, leads to the formation of novel bonds.

1.5. Dichlorodiazadienes as efficient synthones in organic synthesis. The synthesis of (E)/(Z) isomers of methyl 2-phenyl-2-(2-phenylhydrazone)acetate. In our previous researches we showed that, synthesized dichlorodiazadienes are useful synthons for their unical structures. Solvolysis of dichlorodiazadienes in alcohol results with etherisation (scheme 17).



Scheme 14. The synthesis of derivatives of phenylacetic acid

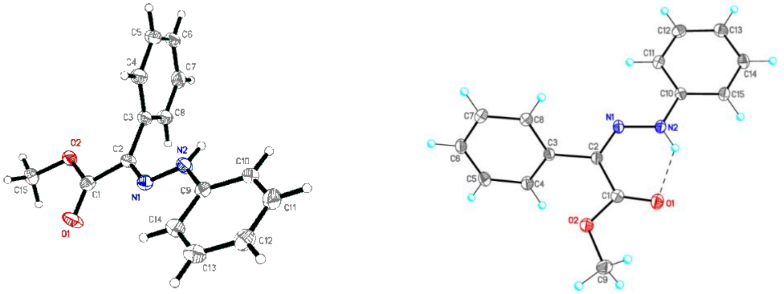


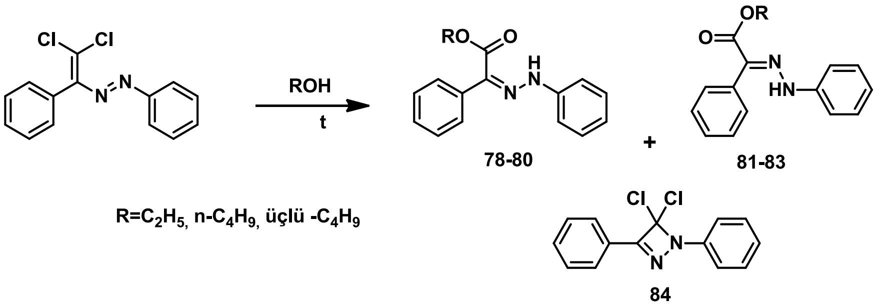
Figure 21. The molecular structure of methyl (Z)/(E)-2-phenyl-2-(2-phenyl-hydrazono)acetate.

It was determined that during the synthesis both of the isomers are obtained and their ratio approximately 1:1. The structures of synthesized compounds was studied by NMR and X-ray single-crystal method.

The synthesized during the reaction (E)/(Z) isomer mixture of methyl-2-phenyl-2-(2-phenyl-hydrazono)acetate was purified by column chromatography and their structure was determined by NMR spectroscopy.

Due to the fact that the NH group in the structure of Z isomer forms a hydrogen bond with COO group, it's signal shifted to the weaker side (12.47 Hz). In case of E isomer due to the fact that hydrogen bond doesn't form, the signal from NH group shifted to the strong side (8.17 Hz) and this proves the formation of both isomer mixture during the reaction.

Due to the fact that obtained compounds didn't demonstrate antimicrobial activity, the reaction of dichlorodiazadienes with various alcohols was studied.



Scheme 15. The transformation reaction of (E)-1-(2,2-dichloro-1-phenyl-vinyl)-2-phenyldiazene

Thus, it was determined that a mixture of hydrozoic derivatives of phenyl acetic acid was obtained as a result of the solvolysis reaction of dichlorodiazadiene synthesized in an alcoholic environment under the conditions of a catalytic olefination reaction.

As a result, it was determined that hydrolysis of dichlorodiazadienes which was obtained in catalytic olefination reaction conditions, leads to the formation of phenylacetic acid hydrozo derivatives mixture in an alcohol medium. In all reactions, 4,4-dichloro-1,3-diphenyl-1,4-dihidro-1,2-diazet (**84**) was gotten besides these isomers. 86 was purified from other compounds by column chromatography.

The study of antimicrobial properties of the synthesized compound was done by twofold microdilution method. For this reason, new compound was dissolved in DMSO (dimethylsulfoxide), 1 mkq/ml solution of it and below given dilutions were prepared. (1:1000, 1:100, 1:10)

Table 1. The antimicrobial activity of synthesized compound

Bacteria	***Staphylococcus aureus***		***Escherichia coli***		***Aspergillus niger***		***Candida albicans***	
The impact of time	24 hours	48 hours	24 hours	48 hours	24 hours	48 hours	24 hours	48 hours
	Inhi bition zone	Inhi-bition zone	Inhi-bition zone	Inhi-bition zone	Inhi-bition zone	Inhi-bition zone	Inhi-bition zone	Inhi-bition zone
1000 mkq	24 mm	36 mm	15 mm	-	12 mm	20 mm	-	-
100 mkq	18 mm	27 mm	10 mm	-	10 mm	16 mm	-	-
10 mkq	12 mm	20 mm	8 mm	-	3 mm	5 mm	-	-

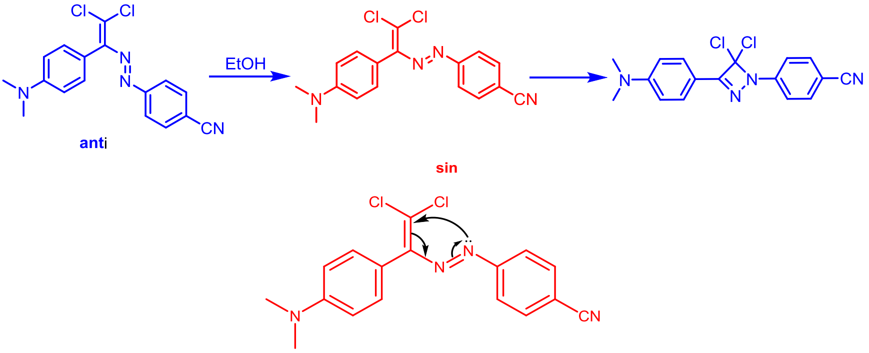
As it can be seen from table 1, newly synthesized compound demonstrate antimicrobial activity, but depending on the nature of microbe it is effect is also different. The highest activity among all bacteria was demonstated against *Staphylococcus aureus* bacteria.

The antimicrobial activity of a novel synthesized compound – legend: 1:1000, 1:100, 1:10 ratios of dilutions: “–” sign demonstrates the absence of antimicrobial activity.

Thus, this compound demonstrates a promised activity against *Staphylococcus aureus* at a ratio 1:1000, in the case of *Aspergillus niger* fungi, this effect was comparatively less. Despite the fact that it has an effect against *Escherichia coli* bacteria, there was no dependence from time. In addition to this, there was no activity against *Candida albicans* fungi.

Thus, considering antibacterial and antifungal activity of studied in microbiological laboratory (Z)-methyl-2-phenyl-2-(2-phenylhydrazono) acetate, it can be advised as an antimicrobial compound.

1.6. Synthesis of diazete derivatives. As it is known from the literature, the compounds that contain azo-group in their structure can be in syn and anti forms and their mutual transitions are possible as mentioned below – from anti to syn by the impact of UV-light, from syn to anti by the impact of temperature. The synthesized dichlorodiazadienes, which structure was confirmed by X-ray single-crystal method, mainly are in anti-form. It was firstly determined by us, that in the presence of ethyl alcohol along with the formation of ester the azide derivative was also obtained, at this time the transformation of anti-form to syn was observed and as a result of intermolecular cyclization the diazide derivative was also obtained.



Scheme 16. The formation of 4-(4,4-dichloro-3-(4-(dimethylamine)phenyl)-1,2-diazete-1(4H)-il benzonytrile

The structue of obtained compounds was determined by X-ray single-crystal method (figure 22).

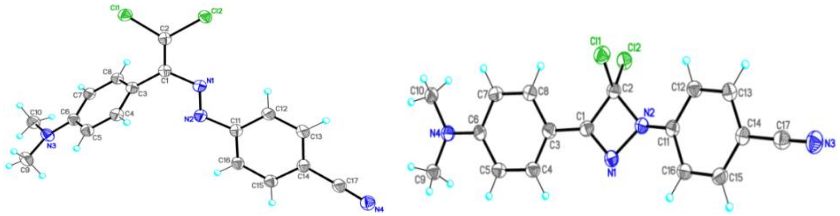


Figure 22. The molecular structure of 65 and 93 compounds

As a result of these reactions, along with modificated acetic acid derivatives, it was possible to obtain microbiologically active diazates.

The third chapter is dedicated to experimental procedures and their conclusions.

CONCLUSIONS

1. The synthesis of corresponding hydrazones on the basis of o, m, and p-nitrobenzaldehyde with various phenylhydrazines and the synthesis of 1.1-dichlorodiazadiene derivatives at COR conditions on the basis of the latter one were performed and on the basis of X-ray single-crystal method investigations, the existence of non-covalent interactions CI···Cl, N···CI, CI···O, π···π, and weak F···π halogene, , CI···π, as well as, CH···F , N···H, O···H was determined.
2. Depending on the position of the nitro group and Cl atoms in the benzene ring, the impact of new non-covalent interactions on crystal design was determined by X-ray single-crystal method.
3. The formation of new non-covalent interactions by the substitution of Cl atoms with an electron-donating methyl group in hydrazine fragment as well as a nitro group by F atoms in an aldehyde fragment in the structure of synthesized dichlorodiazadienes was confirmed.
4. When the strong electrodonor dimethylamine group in the aldehyde fragment was in the hydrazine fragment and the nitrile group in the para state, phenylhydrazones were dimerized on a "head-to-tail" basis, which led to the synthesis of pharmaceuticals as the main product of the reaction.
5. The antimicrobial properties of dichlorodiazadienes which were synthesized on the basis of o,m,p-nitrobenzaldehyde were com-

paratively studied and considering structure-activity dependence the highest antibacterial activity was demonstrated by (E)-1-(2,2-dichloro-1-(3-nitrophenyl)vinyl)-2-(3,5-dimethyl-phenyl)diazene

6. It was determined that the reaction of 1.1-dichlorodiazadienes with alcohols resulted in formation of E/Z isomeric mixture of hydrazono derivatives of phenylacetic acid ester as well as an additional product diazete compounds.

Published scientific papers on dissertation materials

1. Məhərrəmov, A.M. Katalitik olefinləşmə reaksiyası əsasında benzoy aldehidi və bəzi törəmələrinin fenilhidrazonlarından dixlordiazabutadien strukturlu birləşmələrin sintezi / A.M.Məhərrəmov, G.T.Süleymanova, G.V.Babayeva [və b.] // Kimya Problemləri, – Bakı: – 2018. №2, – s. 230-238.

2. Maharramov, A.M. Synthesis and X-ray investigation of nitro, dichlorine derivatives of 1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene by catalytic olefination reaction / A.M.Maharramov, G.T.Suleymanova, Kh.A.Garazadeh [et al.] // Journal of Low Dimensional Systems, – 2018, 2 (1), – p. 37-44.

3. Maharramov, A.M. Synthesıs of dıhalogendıazadıene and farmazan derıvatıves ın the catalytıc olefınızatıon reactıon / A.M.Maharramov, N.G.Shıkhalıev, G.T.Suleymanova [et al.] // Journal of Low Dimensional Systems, – 2018, 2 (2), – p. 24-29.

4. Maharramov, A.M. Pnicogen, halogen and hydrogen bonds in(E)-1-(2,2-dichloro-1-(4-substituted phenyl)vinyl)-2-(2-nitrophenyl)diazenes / A.M.Maharramov, N.Q.Shixaliyev, G.T.Suleymanova [et al.] // Dyes and Pigments, – 2018. Dec; 159. – p. 135-141.

5. Atioğlu, Z. Crystal structure and Hirshfeld surface analysis of (E)-1-(2,2-dichloro-1-(4-nitrophenyl)vinyl)-2-(4-fluorophenyl)-diazene / Z.Atioğlu, M.Akkurt, N.Q.Shikhaliyev [et al.] // Acta Crystallographica, – 2019, 75(2), – p. 237-241.

6. Akkurt, M. Crystal structures and Hirshfeld surface analyses of the two isotypic compounds (E)-1-(4-bromo phenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl] diazene and (E)-1-(4-chloro phenyl)-2-[2,2-dichloro-1-(4-nitrophen-yl)ethenyl] diazene $C_{14}H_8BrCl_2N_3O_2$ and $C_{14}H_8Cl_3N_3O_2$ / M.Akkurt, N.Q.Shikhaliyev, G.T.Suleymanova [et al.] // Acta Crystallographic Communications E, – 2019. Aug; 75(8). – p. 1199-1204.

7. Shikhaliyev, N.G. Synthesis, characterization and antibacterial studies of derivatives / N.G.Shikhaliyev, G.T.Suleymanova, A.A.İsrayilova [et al.] // Arkivoc, – 2019, – part vi, – p. 64-75.

8. Süleymanova, G.T. (Z)-metil-2-fenil-2-(2-fenilhidrazono)asetatın antimikrob xassələrinin tədqiqi // – Bakı: Bakı Mühəndislik Universiteti, – 2018. – №2, – s. 120-122.

9. Süleymanova, G.T. Metil 2-fenil-2-(2-fenilhidrazon)asetatın (E)/(Z) izomerlərinin sintezi // – Bakı: Azərbaycan Milli Elmlər Akademiyasının Gəncə bölməsi, Xəbərlər Məcmuəsi, – 2019. – №3, – s. 64-67.

10. Shikhaliyev N.G., Ahmedova N.E., Mammadova G.Z, Suleymanova G.T, Babayeva G.S, Gurbanov A.V., Garazade Kh.A, Nenajdenko, V.G. Synthesis of dichlorodiazobutadienesfrom nitrobenzaldehydes // The Fourth International Scientific Conference «Advances in Synthesis and Complexing», – RUDN University, – Moscow, Russia: RUDN, – 24-28 April, – 2017, – p. 84.

11. Süleymanova, G.T., Əməş-zadə, Ü.A., Əkbərli, K.E., Muxtarova, S.H., Məmmədova, G.Z., Bağırova, X.N., Şıxaliyev, N.Q., Məhərrəmov, A.M. Benzoy aldehidinin nitro törəmələri əsasında heminal dixlor əvəzli heterodien törəmələrinin sintezi və molekulyar quruluşu // «Kimyanın aktual problemləri» XI Respublika Elmi Konfransı, – Bakı: Bakı Universiteti Nəşriyyatı, – 03-04 may, – 2017, – s. 3.

12. Məhərrəmov, A.M., Süleymanova, G.T., Şıxaliyev, N.Q., Əsgərova, U.F., Muxtarova, S.H., Mikayılova, N.F., Nenaydenko, V.G., Musayev, F.N. Benzoy aldehidinin fenilhidrazonlarından dixlordiazabutadien strukturlu birləşmələrin sintezi // «Kimyanın aktual problemləri» XII Respublika Elmi Konfransı, – Bakı: Bakı Universiteti Nəşriyyatı, – 03-04 may, – 2018, – s. 5-6.

13. Məhərrəmov, A.M., Süleymanova, G.T., Şıxaliyev, N.Q., Babayeva, G.V., Qacar, A.M., Əməş-zadə, Ü.A., Bağırova, X.N., Mehdiyeva, K.N. 1-(2,2-dixlor-1-fenilvinil)-2-fenildiazenin nitro və dixlor törəmələrinin sintezi // «Kimyanın aktual problemləri» XII Respublika Elmi Konfransı, – Bakı: Bakı Universiteti

Nəşriyyatı, – 03-04 may, – 2018, – s. 139-140.

14. Maharramov, A.M., Suleymanova, G.T., Askerova, U.F., Babaeva, G.V., Shikhaliev, N.G., Nenaidenko, V.G. Non-covalent interactions in the reactions of catalytic olefination // The 2nd Struchkov Meeting, International Workshop on Chemical Crystallography and Structural Biology, – RUDN University, Moscow: RUDN, – 13-16 November, – 2018, – s. 77-78.

15. Gurbanova, N.V, Magerramov, A.M., Shikhaliyev, N.G, Suleymanova, G.T., Gurbanov, A.V., Mamedov, İ.G., Babaeva, G.V., Nenajdenko, V.G. Pnycogenic, halogen and hydrogen bonds in (E)-(2,2-dicloro-1-(2-nitrophenyl)vinyl)-2-(para-substituted phenyl)diazenes // The Fifth International Scientific Conference «Advances in Synthesis and Complexing», – RUDN University, – Moscow, Russia: RUDN, – 22-26 April, – 2019, – p. 151.

16. Suleymanova, G.T., Askerova, U.F., Muxatova, S.H., Mamedova, N.A., Mikayilova, N.F., Pirverdiyeva, N.R., Shikhaliyev, N.G. The synthesıs of dichlorodıazadıenes on the basıs of o, m, p-benzaldehyde // The Fifth International Scientific Conference «Advances in Synthesis and Complexing», – RUDN University, – Moscow, Russia: RUDN, – 22-26 April, – 2019, – p. 101.

17. Suleymanova, G.T., Shikhaliyev, N.G., Maharramov, A.M., Ganbarova, C.G., Garazadeh, Kh.A., Niyazova, A.A., Gurbanov, A.V., Nenajdenko V.G.· Synthesis of dichlorod iazadienes on the basis of phenyl hydrazones of 3-nitrobenzoic aldehyde // The Fifth International Scientific Conference «Advances in Synthesis and Complexing», – RUDN University, – Moscow, Russia: RUDN, – 22-26 April, – 2019, – p. 260.

18. Süleymanova, G.T., Babazadə, Ə.Ə., Babayeva, G.V., Şıxaliyeva, I.M., Qarazadə, X.A., Şıxaliyev, N.Q., Məhərrəmov, A.M. (Z)-etil 2-(4-(dimetilamino)fenil)-2-(2-fenilhidrazon)asetat törəmələrinin sintezi // «Kimyanın aktual problemləri» XIII Respublika Elmi Konfransı, – Bakı: Bakı Universiteti Nəşriyyatı, – 15-16 may, – 2019, – s. 338.

19. Süleymanova, G.T., Süleymanov, İ.E., Babazadə, Ə.Ə., Niyazova, A.A., Mehdiyeva, K.N., Şıxaliyev, N.Q. Dixlordiazadienlərın bəzi çevrılmə reaksıyaları // «Kimyanın aktual problemləri» XIII Respublika Elmi Konfransı, – Bakı: Bakı Universiteti

Nəşriyyatı, – 15-16 may, – 2019, – s. 301-302.

20. Сулейманова, Г.Т., Ахмедова, Н.Э., Аскерова, У.Ф., Гаразаде, Х.А., Шахмурадова, А.А., Гусейнова, Л.Р., Бабаева, Г.В., Абдулов, М.С., Шыхалиев, Н.Г. Синтез дихлордиазадиенов на основе 4-нитробензальдегида» // Марковниковский Конгресс по Органической Химии MC150, – Казань-Москва, – Россия: Адмирал Принт, – 21-28 Июнь, – 2019, – р. 230.

21. Süleymanova, G.T., Maharramov, A.M., Babayeva, G.V., Gurbanova, N.V., Şıkaliyev, N.G., Yücel, S. Metil (Z)/(E)-2-fenil-2-(2-fenil-hidrazono)asetatın sintezi // Ulusalalarası kimya kongresi, – İstanbul: – 10-13 sentyabr, – 2019, – s.393.

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