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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**GENERAL CHARACTERISTIC OF THE STUDIES  
OF THE SYNTHESIS OF DICHLOROBUTADIENE  
DERIVATIVES BASED ON THE REACTION OF  
N-SUBSTITUTED HYDRAZONES WITH  
POLYHALOGENOMETANES**

Specialty: 2306.01 – Organic chemistry

Field of science: Chemistry

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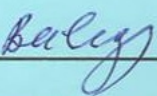
The work was performed at the scientific laboratory of «Thin Organic Chemistry» on the base of department of Organic Chemistry department at Baku State University.

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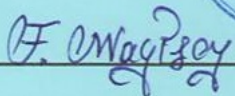
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## THE RELEVANCE OF THE WORK

The development of effective methods for the synthesis of new polyphonic compounds based on catalytic reactions in organic synthesis is one of the urgent issues. These syntheses include the functionalization of any group on the substrate or the introduction of new functional groups, the intramolecular and intermolecular heterocyclic formation of two or more groups, the introduction of new functional groups, use such interesting transformations as C–C, C=C, C=N, C–N, C–Hal, etc. In this regard, the synthesis of dichlorodiazabutadienes, which are chemically active synthons, occurs as a result of the conversion of the carbonyl group  $\text{ArCH=O}$  to the local oscillator, which retains the  $-\text{N}=\text{N}-\text{C}=\text{CCl}_2$  fragment in aromatic aldehydes. Thus, the presence of dichlorodiazabutadienes with a  $\pi$ -electron system of an acceptor conjugated group, as well as a fragment of a dichloride compound in a double bond, opens up wide possibilities for their synthetic use as accessible synthons.

As can be seen from the formula, because of the electron acceptor azo group, azabutadienes have strong electrophilic properties. That is why reactions with various O-, N-, S- and C-nucleophiles, substitution of Cl atoms by nucleophiles and synthesis of heterocycles in different directions with the presence of azo groups allow us to study the synthetic importance of these polyphonic synthons in a wide spectrum.

In addition, these compounds can be used as azo dyes. The  $\text{E} \leftrightarrow \text{Z}$  isomerism resulting from the double bond  $\text{N}=\text{N}$  gives characteristic properties to azo dyes, which further demonstrates the importance of dichlorodiazabutadiene.

Despite the synthesis of many dichlorodiazadines, the synthesis of bis-dichlorodiazadienes and their studies are carried out less. From this point of view, the synthesis of bis-dichlorodiazabutadienes and their synthetic potential are very relevant. Thus, bis-4,4-dichloro-1,2,3-dioxido-1,2,3 dioxide, which is considered an important synthesis from the point of view of catalytic olefination in the reaction of different bis-phenylhydrazones from the reaction of different phenylhydrazines and different bis-hydrazines with different aldehydes. the

synthesis of structural compounds, the study of their synthetic capabilities (reactions with various O-, N-, S- and C-nucleophiles, the replacement of the Cl atom by nucleophiles and the synthesis of bis-heterocycles in various directions by an azo group), as well as physiological activation. The application is of great importance. The preparation of 4-azido-2,5-diaryl-2H-1,2,3-triazole by the reaction of specially synthesized (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenylazine with sodium azide has a large value. At the same time, a small number of chlorine, fluorine and bromine atoms are known in the molecule. In this regard, the synthesis of dichlorodiazabutadiene derivatives, which combines all three halogen atoms, is of great interest in the field of organic synthesis and crystal chemistry. Thus, a comparative study of non-covalent bonds between these atoms in the design of the molecule is very relevant.

Many fundamental chemical processes include the breaking or transformation of strong covalent bonds, which, in turn, require a large expenditure of energy in the thermodynamic and kinetic profile of the reaction. Finding ways to obtain intermediates that require less energy for this purpose is one of the pressing issues facing organic chemists. The use of non-covalent bonds in synthesis is becoming an ever-growing field of research, which suggests that they can be used in organic synthesis, medicine, catalysis, biomolecular and polymer non-composite systems. Non-covalent bonds (O  $\cdots$  B, O  $\cdots$  Si, O  $\cdots$  S, N  $\cdots$  B, N  $\cdots$  N, N  $\cdots$  P, N  $\cdots$  S, Cl  $\cdots$  Cl, organic synthesis, synthesis of metal complexes, formation of single crystals and catalysis) Cl  $\cdots$  N ) has already been proven in specific reactions that play a key role. Since non-covalent interactions affect the structure and energy of the molecule, it also affects the chemical, regio- or stereoselectivity of the reaction. In addition, in the modern world, “young” analogues, such as halogen, melogen and tetral, are used as synthetic agents in the development of new materials and catalysts. In this regard, the study of the role of non-covalent bonds in the synthesized dichlorodiazabutadiene using RQA studies is in the focus of attention of organic chemists in connection with their relevance.

**Object and subject of research.** The object of research is the compounds of mono- and bis-dichlorodiazabutadienes, biologically

active azidotriazoles synthesized from them, in order to show how important these compounds are in the field of organic chemistry. The subject of this research is the role of non-covalent bonds in the design of the molecular structure of mono- and bis-dichlorodiazabutadienes and their application as dyes.

**Purpose of the work.** The main goal of the dissertation is the reaction of mono (derivatives of benzoaldehyde) and dialdehydes (terephthalic, isophthalic and 2,3,5,6-tetrafluoroterephthalaldehydes) with different phenylhydrazines, as well as different bis-hydrazine with aldehydes. Synthesis of 2, 2-dichloro-1-phenylvinyl-2-phenyldiazene and bis-4,4-dichloro-1,2-diazabuta-1,3-diene compounds under the conditions of catalytic olefination. Besides, one of the main purposes is to show how useful dichlorodiazabutadiene compounds are from the points of view of organic chemistry and from the point of view of crystal chemistry, through the comparative study of non-covalent bonds.

To achieve these goals, the following tasks were performed.

- Expanding the possibility of synthetic catalytic olefination reactions to synthesize mono- and bis-dichlorodiazabutadiene compounds
- To determine the role of non-valent interactions ( $\text{Cl}\cdots\text{Cl}$ ,  $\text{Cl}\cdots\text{F}$ ,  $\text{N}\cdots\text{Cl}$ ,  $\text{Cl}\cdots\text{O}$ ,  $\text{F}\cdots\text{H}$  and  $\pi\cdots\pi$ ,  $\text{Cl}\cdots\pi$ ) in design of single crystals of phenylhydrazines and reaction products with the help of X-ray structural analysis (RQA), as well as the use of synthesized compounds as azo dyes and research of physiological activity of these compounds;
- Mononuclear synthesis physiologically active 4-azido-2,5-diaryl-2H-1,2,3 triazoles from the reaction of sodium azide with (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene- and for comparative research of non-valent bonds on the basis of 1- (4-bromophenyl) -2- (2,2-dichloro-1- (4-fluorophenyl) vinyl) diene molecules, which at the same time. contain chlorine, fluorine and bromine

**Research methods.** Syntheses were carried out in the "Fine-Organic Synthesis" ETL by appropriate methods. The crystal structures of the synthesized compounds were confirmed by the Bruker

APEX II CCD diffractometer. NMR <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker Avance spectrometer in CDCl<sub>3</sub> and DMSO solvents. UT-254 was performed on NTX Silufol board, the formed spots were examined in UV lamp beams. Column chromatography was performed using Merck silicogel. Mass spectrum (ESI-MS) was determined by spectroscopy. Elemental analysis was performed on the Carlo Erba analyzer.

**The main provisions:**

- synthesize new mono- and bis-dichlorodiazabutadienes under the conditions of catalytic olefination reaction;
- Study of non-covalent bonds in the crystal structure of the synthesized compounds;
- demonstration of synthetic potential synthesized dichlorodiazabutadiene;
- Application of bis-dichlorodiazabutadienes as a dye.

**Scientific novelty.** Under the conditions of catalytic olefination of benzoic aldehyde, the corresponding (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene was synthesized, and the presence of intermolecular non-covalent Cl...Cl bonds in its molecular structure was determined by X-ray diffraction studies.

Physiologically active 2H-1,2,3-triazoles were synthesized in one step by the reaction of derivatives of synthesized dichlorodiazabutadiene with sodium azides.

A comparative analysis of the synthesis of 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl) diazene, which combines the atoms of chlorine, fluorine and bromine, as well as non-covalent bonds based on them, was carried out .

For the first time, the synthesis of derivatives of 4,4-dichloro-1,2-diazabutadiene was carried out under the conditions of the catalytic olefination of aromatic dialdehydes (terephthalic, isophthalic and 2,3,5,6-tetrafluoroterephthalic) bis-phenylhydrazones in the presence of CuCl catalyst.

The stereochemical properties of the reactions were investigated by NMR, and it was found that all reactions are observed mainly with the formation of E-isomers.

And in the case of the presence of 2,3,5,6-tetrafluoroterephthalal-

dehyde, the presence of non-covalent ( $\text{Cl}\cdots\text{F}$ ,  $\text{F}\cdots\text{H}$ ,  $\text{Cl}\cdots\pi$ ) bonds was determined by X-ray diffraction analysis. In addition, the influence of functional groups on crystal design was studied.

The use of synthesized during the reactions carried out on the basis of bis (4-hydrazinylphenyl) methane with the corresponding hydrazones obtained was studied, bis-(4-((E)-2,2-dichloro-1-(4-phenyl vinyl) diazenyl) phenyl) as azo dyes. The predominance of E isomers in compounds of this type was formed due to intramolecular  $\text{N}\cdots\text{Cl}$  and intermolecular hydrogen, halogen and chalcogen bonds.

During the study of the antimicrobial properties of the synthesized (E)-1-(2,2-dichloro-1-phenylvinyl)-2-diazenin, it was found that this compound can effectively act against *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Candida albicans*.

Using the Hirschfeld surface analysis method, it was found that the  $\text{C}-\text{Br}\cdots\text{Cl}$ ,  $\text{C}-\text{Cl}\cdots\text{Br}$ ,  $\text{C}-\text{H}\cdots\text{Cl}$  halogen bonds in this crystal play an important role in the formation of the crystal structure. In addition, it was found that weak  $\text{N}\cdots\text{H}$  dipole-dipole interactions and  $\pi-\pi$  interactions also play a role in the formation of this structure.

**The practical importance of the work.** Due to the fact that the synthesized compounds are polyhalogen-containing compounds, their use as a model for studying certain parameters of non-covalent interactions (halogen, chalcogen, tetra,  $\pi\cdots\pi$ ) is of great importance. Due to the fact that the synthesized compounds are multifunctional in nature, due to the presence of heminal chlorine atoms, azo groups, various functional groups in the benzene ring, from the point of view of organic synthesis, they can be used as synthons to obtain various important compounds. Azo dyes can be used in the manufacture of dyes used in weaving, cosmetics, substances used in the printing industry, drugs, food colors, liquid crystals, optoelectronic systems, etc.

**Applicant's personal contribution to the research.** The author made an indirect contribution to the implementation of the dissertation and the solution of the submitted questions. She took an active part in the composition of the latest literature in the field of world literature, in conducting experiments and in the analysis of the spectra of NMR products of reactions. She shared ideas, results and wrote articles with the participation of specialists in relevant fields (organic

chemists, biologists, etc.).

**Published labors.** The main parts of the work were presented at international and republican conferences held in Russia, Azerbaijan:

- X, XI, XII Republican Scientific Conferences "Actual problems of chemistry" (Baku, 2016, 2017, 2018);
- Markovnik reading. Organic Chemistry: from Markovnikova to our days School-conference of young scientists "Organic Chemistry: Traditions and Modernity" (Moscow, 2017, 2019);
- V Conference on the chemistry of heterocyclic "New directions in the chemistry of heterocyclic compounds" and XXI School-conference on organic chemistry, dedicated to the 120th anniversary of the birth of Academician of the USSR I.Ya. Postovskogo in the framework of the V All-Russian Conference on Organic Chemistry (with international participation) (Russia, Vladikavkaz, 2018);
- The Fourth International Scientific Conference «Advances in Synthesis and Complexing» (Moscow, 2017).

On the topic of the dissertation published 17 scientific papers, including 8 articles and 9 conference materials.

**The structure of the dissertation.** The dissertation consists of an Introduction, 3 chapters, a conclusion and a list of references, covering 187 pages in A4 format. The main part of the work (excluding figures, tables, graphs and bibliography) is 166 659 (including Introduction – 12 971, Chapter I – 57 626, Chapter II – 62 979, Chapter III – 30 871, Conclusion – 12 971). The list of used literature includes 281 sources cited in the dissertation. The dissertation contains 19 tables and 60 figures.

The *introduction* substantiates the relevance, purpose, scientific novelty and practical importance of the work.

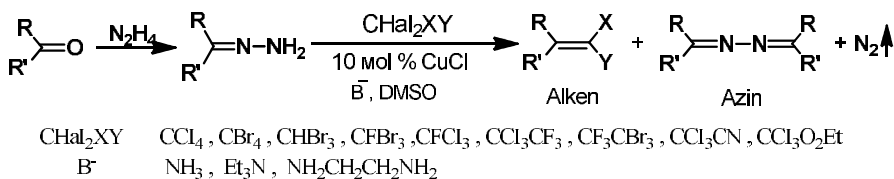
The *first chapter* provides information on hydrazines, hydrazones, triazoles, non-covalent bonds.

The *second chapter* is devoted to mono, bis dichlorodiazabutadiene, triazole antimicrobial, Hirschfeld, the *third chapter* is devoted to the experimental part of the research work and the confirmation of the results by physical research methods.



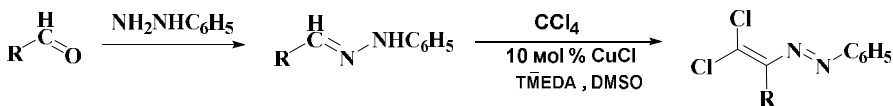
## MAIN CONTENT OF WORK

**Synthesis of dihalo-diazadienes under the conditions of a catalytic olefination reaction.** The catalytic olefination reaction is based on the synthesis of the corresponding geminal dihalogen-substituted olefins from the reactions of various N-substituted hydrazones with aldehydes and ketones in a basic medium in a catalytic amount of CuCl with various polyhaloalkanes. The reaction is followed by the formation of azines as a by-product and the evolution of nitrogen.



### General scheme of the catalytic olefination reaction

The dissertation is mainly based on the synthesis of 4 structural compounds under the conditions of catalytic olefination of N-substituted phenylhydrazones. As a result of the reaction, important dichlorodiazabutadiene synthones in the presence of TMDEA in the amount of CuCl catalyst were obtained. In other words, the C=O group was converted to a heterodiene, which retained the  $-\text{N}=\text{N}-\text{C}=\text{C}<$  fragment.



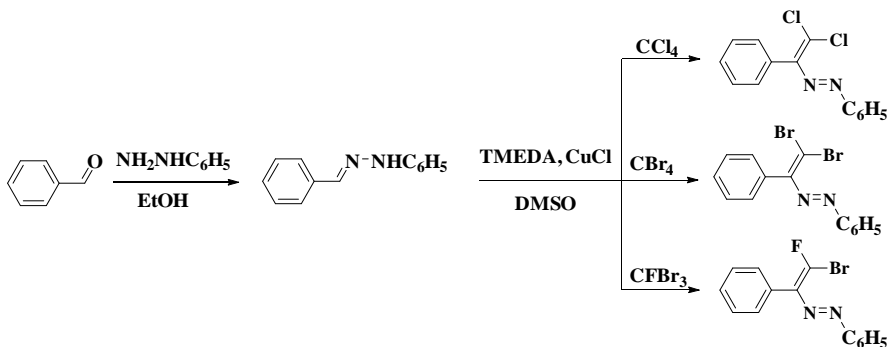
### Synthesis of Dichlorodiazabutadiene from Phenylhydrazone

The presence of two functional reaction centers in the reaction product, both the heminal of the halogen-substituted double bond and the azo group (attached dichlorodiazabutadiene) ones, shows their great importance from the point of view of organic synthesis. And as can be seen from the structure, the carbon atom holding the heminal chlorine atoms plays the role of an electrophilic center. It is from this point of view that they can be used in the synthesis of new physiologically active classes of compounds in reactions with various nucleophilic reagents.

In addition, dichlorodiazabutadiene can be used in fine organic

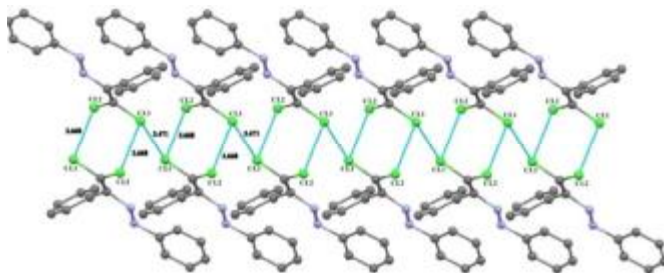
synthesis for the synthesis of various heterocycles (especially derivatives of 2H-1,2,3-triazole and pyridazine), complex compounds, azo dyes, which shows the relevance of dichlorodiazabutadiene. The physiological activity of these compounds and their use as azo dyes in analytical chemistry should also be especially noted.

**Synthesis of dihalo-diazadienes based on benzylidene-2-phenylhydrazine.** Based on the reactions of phenylhydrazone synthesized based on benzoic aldehyde with polyhalogen metans ( $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CFBr}_3$ ), the corresponding compounds were synthesized and their structure was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.



#### Synthesis of (E)-1-(2,2-dihalo-1-phenylvinyl)-2-phenyldiazenes

Besides, a single crystal of (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene was obtained and the presence of non-covalent  $\text{Cl}\cdots\text{Cl}$  bonds between the molecules was determined and confirmed by X-ray diffraction method.



Intermolecular non-covalent  $\text{Cl}\cdots\text{Cl}$  bonds are indicated by a dashed line.

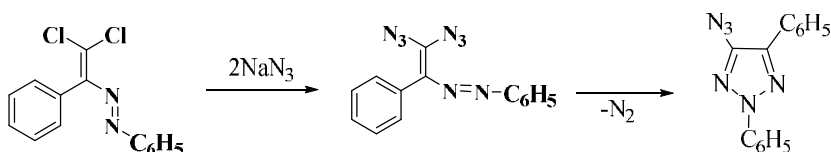
Very little information is found in the literature on the synthesis

and reactivity of diazabutadiene. However, on the other hand, the possession of a large synthetic potential of these compounds, their manifestation of high physiological activity from the point of view of organic synthesis, makes it possible to use them as important synth.

Taking into account all the above, we investigated the antimicrobial properties of the simplest synthesized compound-(E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene. To this end, 1% solution of (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyl-diazene in ethyl alcohol is diluted in distilled water in the ratios of 1:100, 1:200, 1:400, 1:600, 1:800 (1,2,3,4). Non-covalent Cl-Cl bonds are indicated by dashed lines the antimicrobial properties of (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene have been studied in comparison with widely used drugs such as ethyl alcohol, furacilin and nitrofungin. Gram-positive microorganism – *Staphylococcus aureus*, gram-negative – *Pseudomonas aeruginosa*, *Escherichia coli*, fungal – *Candida albicans* were used as a test culture. For the inoculation of bacteria, MPA (meat-peptone agar), and for the inoculation of fungi – Saburo agar were used. Bacteria inoculation was carried out under the conditions of a thermostat, for 24 hours at a temperature of plus 37°C, and for fungi for 48 hours at a temperature of 28°C. For each test glass, one drop of emulsion was added, containing 500 ml of microbial particles per 1ml, and inoculation was carried out every 10-20 minutes for 1 hour. According to the analysis of the data of Table 1, the synthesized compound has a strong antimicrobial effect on the investigated microorganisms, and for all investigated microorganisms in the samples 1,2,3 regardless of time. So, even at a dilution of 1:800 (sample 4), it completely destroys staphylococcus and E. coli after 20 minutes. With respect to candida, a decrease in the development rate after 10 minutes at a ratio of 1:200 and 20 minutes at 1:400 was observed. The antimicrobial properties of this compound were also studied by the method of disk diffusion. A suspension was prepared from the daily culture (containing 1ml of 1 ml/g of microbial cells). Further, in a Petri dish with MPA, this suspension was added and distributed within this nutrient medium. *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli* formed a 30 mm sterile zone, in *Candida albicans* – 20 mm sterile area. Thus, the (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene synthesized by us is an active bactericidal and fungicidal preparation.

Note that a large number of drugs contain a fragment of 1,2,3-triazole. Triazoles have high biological activity, they are also used against excretion: as an antiplatelet, antimicrobial, antituberculosis, against viruses and microbes, as well as other diseases. Given this,

the preparation of 2H-1,2,3-triazoles is of significant importance from the point of view of organic synthesis. They are compounds with high biological activity, and also used against secretions, as antiplatelet, antimicrobial, as well as against tuberculosis and the treatment of many other diseases. Due to the commercial success of some triazole ring-based drugs, many firms and research groups are interested in developing a new method for synthesizing triazole-containing compounds and analyzing their biological activity. In addition, 1,2,3-triazoles are widely used in the treatment of various diseases. For example, antifungal drugs such as itraconazole, fluconazole, voriconazole, the antiviral drug ribavirin and nutritinib (used in the treatment of breast, bladder, kidney and prostate cancer) containing a triazole ring are known. Ribavirin is a drug used to treat viral diseases such as herpes and hepatitis.

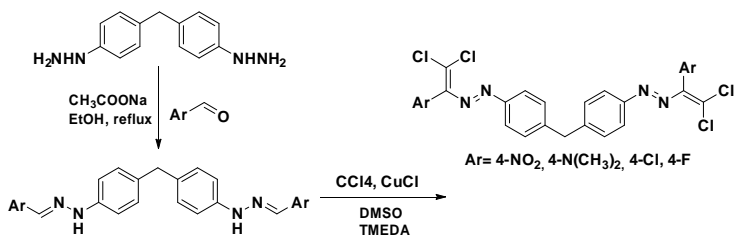


Synthesis of 4-azido-2,5-diphenyl-2H-1,2,3-triazole

Thus, according to the indicated scheme, using simple starting compounds, the formation of a triazole molecule of a rather complex structure containing substituents occurred under predetermined conditions.

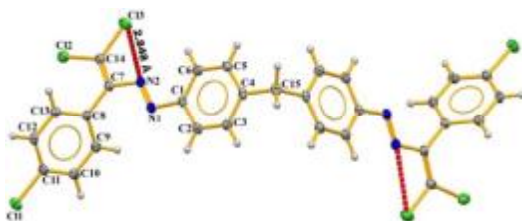
At this time, it seems possible to simultaneously form 5 chemical bonds, and our previous experiments have shown that all these reactions can be carried out sequentially in one flask, without separating the intermediate compounds. Here, the catalytic amount of CuCl used in the first step interferes with heterocyclization. After determining the 2-substituted starting hydrazine in the structure of the obtained triazole and 5-substituted in the structure of the aldehyde, a large number of biologically active 2H-1,2,3-triazole derivatives can be synthesized using various aldehydes and phenylhydrazines. Thus, a tandem conversion of dichlorodiazadienes synthesized on the basis of a new catalytic olefination reaction into 2-substituted-1,2,3-triazole was carried out.

**Synthesis and molecular structure of bis-dichlorodiaza-butadiene.** In recent years, most of the research in the field of halogen bonds is based on non-covalent interactions between molecules and also within molecules, which is apparently due to the large amount of experimental data and the relative simplicity of theoretical calculations. In order to study halogen and hydrogen interactions in the syntheses resulting from halogen-halogen interactions using the reaction of benzoic aldehyde derivatives with bis (4-hydrazinyl phenyl) methane, we synthesized the corresponding bis-dichlorodiaza-butadiene.

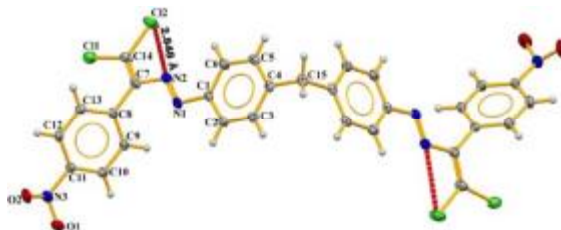


Synthesis of dihydrazine-based bisdichlorodiaza-butadiene derivatives

Crystals of bis (4-((E)-2,2-dichloro-1-(4-nitrophenyl) vinyl) diazenyl) phenyl) methane and bis(4-((E)-2,2-dichloro-1-(4-chlorophenyl) vinyl) diazenyl) phenyl) methane, and their structure was confirmed by XRD.



Bis{4-[(E)-2,2-dichloro-1-(4-nitrophenyl)vinyl]diazenyl} phenyl} methane (**13**)



Bis (4-((E)-2,2-dichloro-1-(4-chlorophenyl) vinyl) diazenyl) phenyl) methane (**14**)

X-ray diffraction analysis of 13 and 14 proves that in the solid state the E-isomeric form is stable. This stabilization is the cause of intramolecular tetral and intermolecular hydrogen and halogen bonds. In the intramolecular tetral bond at 13 and 14, the angles N=N ... Cl and the distance N ... Cl are up to 172.32 Å and 2.848 Å, and each of these distances is less than the sum of the Van der Waals radii of the interacting atoms (N + Cl=1.55 + 1.75=3.30 Å). In addition, 13 and 14 include intermolecular halogen bonds Cl...Cl and O...Cl with lengths of 3.464 and 2.958 Å, respectively; and the length of each of them is less than the sum of the van der Waals radii of the interacting atoms (Cl + Cl=1.75 + 1.75=3.5 Å and O + Cl=1.52 + 1.25=3.27 Å) and the angles Cl-Cl...Cl and Cl-Cl...O are respectively 176.670 and 170.080. At 14, the electron pair of the O (2) atom of the nitro group, acting as an electron acceptor, interacting with the  $\pi$ -system of the adjacent aromatic ring, creates an intermolecular non-covalent ...  $\pi$  bond (length 3.754 Å). In general, both structures are stabilized by multiplet intermolecular hydrogen bonds.

**Bis (4-((E)-(2,2-dichloro-1-(4-substituted phenyl)vinyl)diazetyl) phenyl) methanes as dyes.** Non-covalent interactions affect both the structural energy of the molecule and the chemo-, regio-, or stereoselectivity of the reaction. In recent years, due to the role of nucleic acids in structural biology and their participation in catalysis, chemists have studied their hydrogen bonds and stacking ( $\pi$ ... $\pi$  interactions) in more detail. In addition, in the modern period, “young” interactions like halogen, chalcogen and tetral are used as synthetic agents in the design of new synthetic materials and catalysts. Azo dyes are also used in the preparation of dyes used in weaving, cosmetics, substances used in the printing industry, drugs, food colors, liquid crystals, optoelectronic systems, etc. in addition, the isomerization of E $\leftrightarrow$ Z arising in the double bond N=N gives the azo dyes characteristic properties.

Due to the fact that each isomer exhibits different properties of E $\leftrightarrow$ Z, isomerization is of particular interest. In general, the trans (E) isomer is more stable from a thermodynamic point of view (12 ~ kcal mol<sup>-1</sup>). Due to the presence of an energy barrier (12 ~ kcal mol<sup>-1</sup>) in the photoexcited state of cis (Z) and trans (E) isomers, the trans iso-

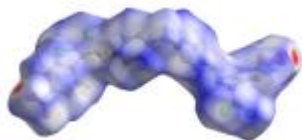
mer predominates at room temperature.

Using light of the appropriate wavelength, solvent, pH, substituent, etc. it is possible to regulate the E $\leftrightarrow$ Z or Z E transformations; however, no regulation of this process by halogen and hydrogen bonds has been found. From this point of view, the role of these bonds in the formation of the E isomer in bis (4-((E)-2,2-dichloro-1-(4-substituted phenyl)vinyl)diazenyl)phenyl methane dyes should be especially noted. Although many azo dyes have been synthesized, bis (azo dyes) are relatively smaller. In addition, the functional properties of azo dyes having halogen, chalcogen and tetral donor centers can be controlled through these interactions. Therefore, the synthesis of new bis (4-((E)-2,2-dichloro-1-(4-substituted phenyl)vinyl) diazenyl) phenyl methane dyes having halogen and hydrogen bonds is very important.

Thus, under the conditions of the catalytic olefination reaction of a pair of benzoic aldehyde derivatives from bis-hydrazone, we synthesized compounds that are important from the point of view of organic synthesis, as well as crystal chemistry, coloring substances, which shows the presence of many new synthetic possibilities of RCO (catalytic olefination reaction).

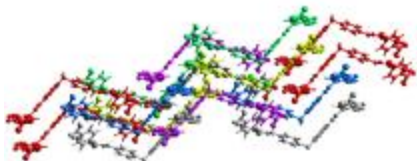
**Hirschfeld surface analysis bis-(4-((E)-(2,2-dichloro-1-(4-nitrophenyl) vinyl) diazenyl) phenyl) methane.** The Hirschfeld surface and fingerprints were taken on the basis of the crystallographic information file (CIF) using CrystalExplorer. The  $d_{\text{norm}}$  of the compounds obtained by us varies in the range of 0.2412–1.2981 Å, the formal index in the range of -1.0000 and 1.0000 Å, and the curvature in the range of -4.0000 and 4.0000 Å. In this crystal, halogen bonds N–O $\cdots$ Cl, hydrogen bonds N–O $\cdots$ H and strong N–O $\cdots$ C interactions,  $\pi\cdots\pi$  stacking interactions play an important main role in the formation of the crystal structure. In addition, the presence of also weak N–O $\cdots$ C, N–N $\cdots$ H, N–C $\cdots$ H dipole – dipole interactions shows the weakness of the interactions, and  $\pi$ – $\pi$  interactions play a role in the formation of this structure.

The presence of N–O $\cdots$ Cl halogen bonds, N–O $\cdots$ H hydrogen bonds, and N–O $\cdots$ C, N–O $\cdots$ C, NN $\cdots$ H, NC $\cdots$ H interactions between the molecules in the crystal was confirmed.



$d_{\text{norm}}$  of the compounds obtained by us in the range from -0.2412 to 1.298 refers to the three-dimensional Hirschfeld surface.

We calculated the total energy of interactions of a chosen randomly selected molecule with a neighboring molecule. Now imagine the calculated values of the interaction energy of an arbitrarily selected molecule with all neighboring molecules. Here, the selected molecule is colored relatively black, and the other molecules are each in a different color, and the energy values corresponding to the colors in the table show the total energy between the molecules



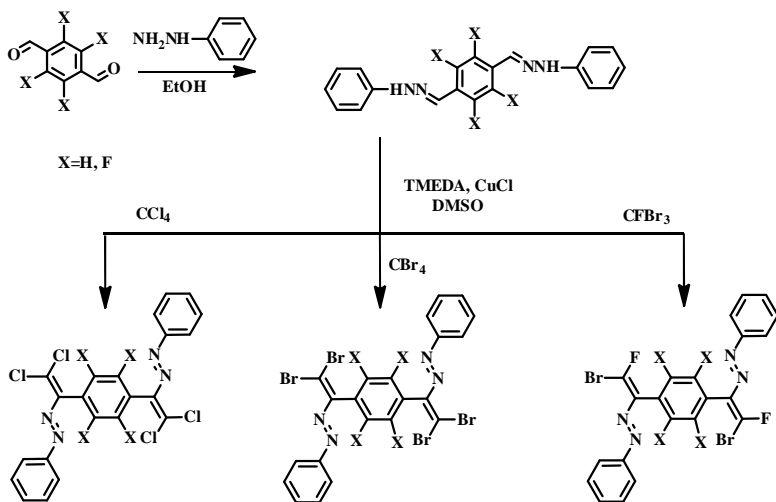
The molecules around the selected (black) molecule are shown in different colors.

	N	Symmetry operation	R	$E_{\text{ele}}$	$E_{\text{pol}}$	$E_{\text{dis}}$	$E_{\text{exc}}$	$E_{\text{full}}$	Symmetry operation
	4	$x+1/2, y+1/2, z$	21.19	HF/3-21G	-67.9	-16.9	-21.1	15.3	-86.8
	2	$-x, -y, -z$	10.23	HF/3-21G	41.0	-16.8	-28.4	18.4	21.1
	2	$-x, -y, -z$	11.41	HF/3-21G	23.6	-8.9	-17.5	10.3	10.9
	2	$-x+1/2, -y+1/2, -z$	16.54	HF/3-21G	-247.0	-143.4	-38.8	16.2	-366.9
	2	$x, y, z$	4.36	HF/3-21G	300.0	-117.3	-169.8	74.2	136.5

The interaction energies (kJ/mol) between the corresponding black molecule with molecules of a different color were calculated on the HF/3-21G model using the Crystal Explorer program.

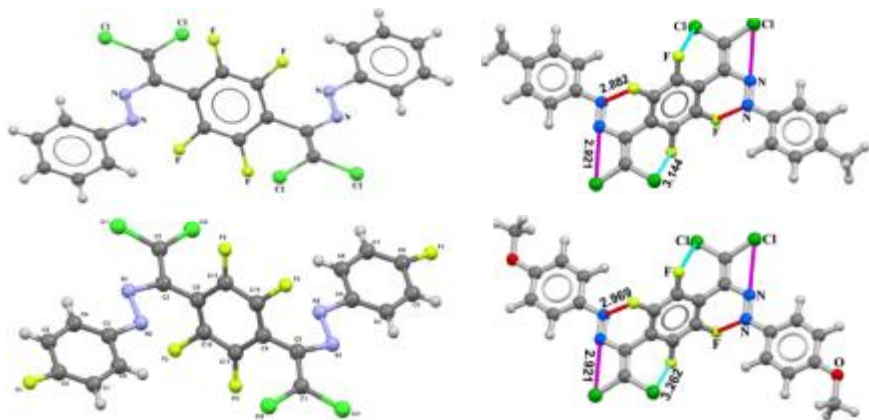
**Synthesis of bis-dichlorodiazadienes under the conditions of a catalytic olefination reaction.** For the behavior of these reactions on terephthalic and tetrafluoroterephthalic aldehydes, the corresponding bis-phenylhydrazones and polyhalogen metans ( $\text{CCl}_4$ ,  $\text{CBr}_4$ ,  $\text{CFBr}_3$ ) were first synthesized by catalytic olefination reactions.





Catalytic olefination reaction of terephthalic and tetrafluoroterephthalic bis-phenylhydrazones

The molecular structure of the reaction products was confirmed by X-ray diffraction method.



The presence of intermolecular non-covalent halogen-halogen ( $\text{Cl}\cdots\text{F}$ ) bonds, intermolecular  $\text{F}\cdots\text{H}$  hydrogen bonds, and  $\text{Cl}\rightarrow\pi$  interactions in the crystal packing was determined. The formation of single crystals in the case of tetrafluoroterephthalic aldehyde from products obtained during reactions with terephthalic and tetrafluoroterephthalaldehydes once again precisely confirms the presence

of intermolecular halogen-halogen bonds in these compounds.

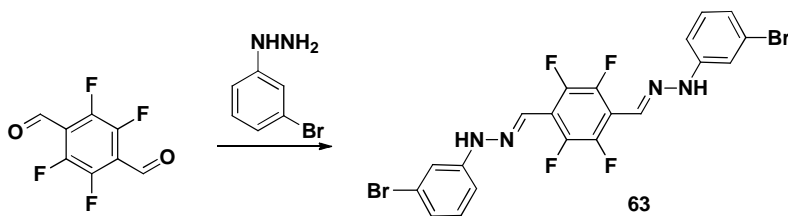
The field of application of the synthesized tetrafluoro compounds as azo dyes was also studied. Azo dyes have a wide range of applications, like photosensitive paints in sensors, ligands, liquid crystals, to preserve the optical properties of data, in flowering materials, nonlinear optics, etc. These properties of azo dyes strongly depend on the presence of the  $-N=N-$  group in the synthon. Depending on the amount of this group ( $-N=N-$ ), azo dyes are divided into mono, bis, and triazo dyes. Compared with mono azo dyes, the amount of bis, tris and polyazo dyes is less. In addition, halogen-containing azo dyes increase their interest due to their good solubility, the manifestation of photoactivity in the solid state, heat and oxidation stability, and also due to the presence of non-covalent bonds. Unlike the hydrogen bond, the halogen bond is considered the most beneficial means of non-covalent rearrangement of functional materials due to specific molecular interactions. Recent theoretical and experimental studies allow a better understanding of the interactions that bind halogen atoms in crystalline engineering, solvent chemistry, optoelectronic materials, catalysis, liquid crystals, in the determination of anions, supramolecular gels, capture and release of small molecules, as well as in biological systems. In practice, non-covalent  $\pi-\pi$ ,  $C-F\cdots H$ ,  $F\cdots F$ ,  $C-F\cdots\pi$ ,  $C-F\cdots\pi$ ,  $C-F\cdots M^+$ ,  $C-F\cdots C=O$  and anion  $-\pi$  interactions, as well as  $F$  – non-covalent interactions are of great interest in the formation and design of single crystals, the formation of functional materials. In aromatic compounds, the introduction of an F substituent in the aromatic ring or the presence of 4 fluorine terephthalic aldehyde having an aromatic ring gives new properties to the compound. These new properties arise due to the high elasticity of the  $C-F$  bond and the above non-covalent bonds, polar and steric effects. Recently, perfluorinated aromatic compounds are widely used in crystalline engineering in mono-azo dyes, catalysis, or coordination compounds. Despite this, there is little information on perfluorinated azo dyes and their synthesis. By introducing electron-donating ( $-OCH_3$ ,  $-CH_3$ ) and electron-withdrawing ( $-F$ ) groups into the aromatic fragment 54, 60-62, it is possible to determine the probability of a bond between the  $S_p$ -para pair of the substituted Hammett constant, as well as the stability of intermolecular halogen bonds.

The solvatochromic properties of bis-azo dyes were studied in three different organic solvents (dichloromethane, dimethylformamide and methanol) with a different polarization index at a temperature of 298 K. For all dyes, 3 absorption peaks were observed in the range of 211-233, 263-327 and 341-381 nm. The first band can be related to the excited electrons of the C=C bond in the olefin fragment. The second UV absorption band can be related to the  $\pi \rightarrow \pi^*$  transition in the aromatic and perfluoroaromatic nuclei. And the third band can be related to the  $\pi \rightarrow \pi^*$  transition in the N=N bond, as well as to intermolecular non-covalent bonds, such as hydrogen, Cl $\cdots$ O, Cl $\cdots$ F, F $\cdots$ Cl and F $\cdots$ F bondings. In general, the introduction of electron-donating ( $-\text{OSH}_3$ ,  $-\text{CH}_3$ ) and electron withdrawing ( $-\text{F}$ ) groups into the aromatic fragment leads to bathochromic and hypsochrome glides in the UV bands, respectively. However, in bis-azo dyes subjected to radiation, there is no such relationship between  $I_{\text{max}}$  and the properties of electrons. With decreasing solvent polarity, the absorption intensity in bis azo dyes,  $\text{MeOH} < \text{DMF} < \text{CH}_2\text{Cl}_2$ , increases.

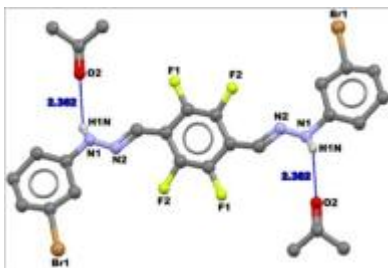
Considering the results obtained, we carried out similar reactions with isophthalic aldehyde. The structure of the synthesized compounds was confirmed by NMR.

**The reaction of bis- (3-bromophenyl) hydrazone with polyhalogen metans.** The reaction of 2,3,5,6-tetrafluoroterephthalaldehyde was investigated under the conditions of catalytic olefination of N-substituted bis-(3-bromophenyl) hydrazone. The presence of fluorine, bromine and chlorine atoms in the synthesized bis-phenylhydrazone and the production of bis-dichlorodiazabutadiene containing fluorine, bromine and chlorine atoms during olefination allow us to conduct comparative studies of non-covalent bonds.

Phenyl hydrazone was first synthesized.



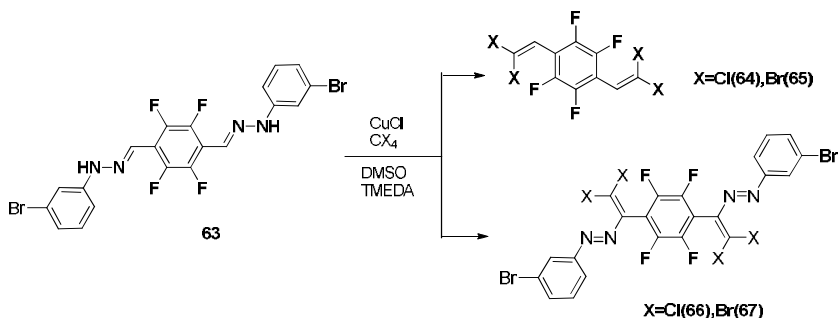
Synthesis of bis- (3-bromophenyl) hydrazone **63**



The formation of a hydrogen bond (2.362 Å) between the acetone molecules and the hydrogen atoms of the imine group  $\text{NH}\cdots\text{O}=\text{C}(\text{CH}_3)_2$  in the crystal of bis-(3-bromophenyl) hydrazone was associated with the participation in the formation of the crystal, which was studied by X-ray diffraction. Also during NMR,  $^1\text{H}$  (DMSO- $d_6$ ; d) analysis, NH protons are observed in the 11.08 region, and N=CH proton is observed in the 7.87 region. In the spectrum at section 2.08, signals belonging to acetone were observed.

As a result of NMR and XRD studies of the reaction with bis-(3-bromophenyl) hydrazone, in addition to the expected products of the corresponding reaction, NMR revealed the formation of vinyl derivatives such as 1,4-bis (2,2-dichlorovinyl)-2,3,5, 6-tetrafluorobenzene and 1,4-bis-(2,2-dibromovinyl)-2,3,5,6-tetrafluorobenzene. Thus, as a result of NMR and XRD studies of the reaction with bis-(3-bromophenyl) hydrazone, in addition to the expected products of the corresponding reaction, NMR revealed the formation of vinyl derivatives such as 1,4-bis (2,2-dichlorovinyl)-2,3, 5,6-tetrafluorobenzene and 1,4-bis-(2,2-dibromovinyl)-2,3,5,6-tetrafluorobenzene. Thus, during the  $^1\text{H}$  NMR analysis of the reaction mixture, in addition to observing 7.25 and 7.31-7.61  $^1\text{H}$  signals belonging to the aromatic nucleus in the 1,4-bis (2,2-dichlorovinyl)-2,3,5,6-tetrafluorobenzene hydrazone fragment, the observation of signals belonging to the vinyl proton (C=CH) in the region of 6.65, as well as the observation of =CH of  $^{13}\text{C}$  NMR signals in the region of 113.9 and =CCl<sub>2</sub> of the signal in the region of 129.9 indicates the formation of 1,4-bis (2,2-dichlorovinyl)-2,3,5,6-tetrafluorobenzene during the reaction. Also, during the reaction carried out with CBr<sub>4</sub>, C=CH proton signals belonging to 1,4-bis (2,2-dibromovinyl)-2,3,5,6-tetrafluorobenzene were observed in the region of 7.23, and in the  $^{13}\text{C}=\text{CH}$  in the NMR spectrum signals – in the region of 116.1 and 123.6, the signal belonging to the =CBr<sub>2</sub> group was observed in the region of 99.7. And this con-

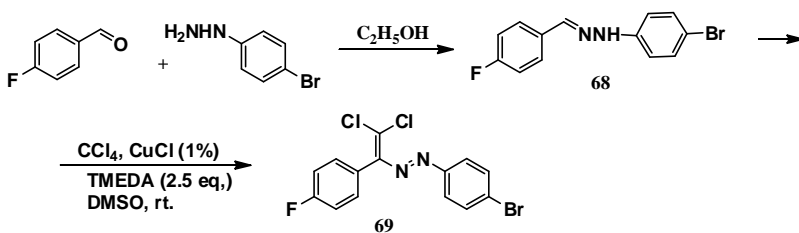
firmly that, in addition to the dihalogenodiazobutadiene derivatives of dihalogenovinyl, the reaction also results.



The reaction of bis-(3-bromophenyl) hydrazone with polyhalogen metanes

As a result of X-ray diffraction analysis for the presence of intermolecular halogen-halogen non-covalent bonds in the synthesized compounds, it was determined that in the crystal structure there are only intermolecular halogen  $\text{Br}\cdots\text{Br}$  bonds (3.869 Å) and  $\text{C}-\text{Br}\cdots\text{Br}$  angles are 176.67° and 170.08°, respectively.

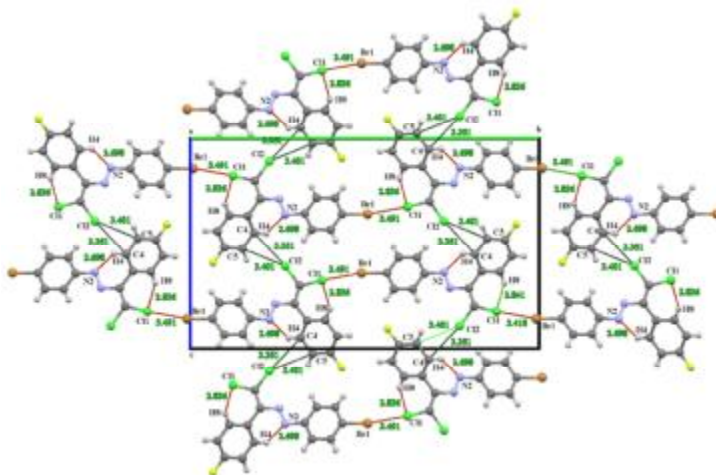
**RSA studies of 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl)vinyl)diazene.** Few compounds are known in which there are simultaneously chlorine, fluorine and bromine atoms. From this point of view, the synthesis of dichlorodiazabutadiene derivatives, combining all three halogens, is of great interest from the point of view of organic synthesis and crystal chemistry. Thus, a comparative study of non-covalent bonds formed in the design of a molecule between these atoms is an extremely urgent task. For this reason, we synthesized dichlorodiazabutadiene containing a fluorine atom in the aldehyde fragment, and a Br atom in the phenylhydrazine fragment. Thus, initially the use of halogen derivatives leads to the formation of new non-covalent interactions, which allows them to be used as a model in the study of halogen-halogen bonds. First, the corresponding phenyl hydrazone was synthesized from 4-bromobenzaldehyde with 4-bromophenylhydrazine and, under the reaction conditions, under the conditions of catalytic olefination, 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl)vinyl was synthesized)diazene.



Synthesis of 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl) diazene

During the analysis of non-covalent bonds in the synthesized 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl) diazene, only the presence of  $Br \cdots Cl$  intermolecular halogen bonds was determined by RGA ( $3.418 \text{ \AA}$  v  $3.491 \text{ \AA}$ ).

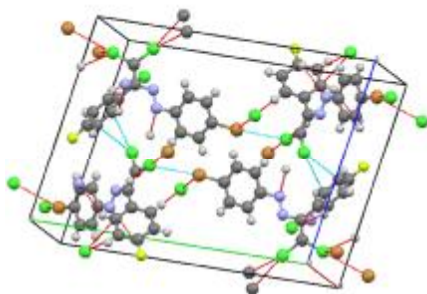
As can be seen from the figure, fluorine atoms do not participate in any non-covalent bond. However, due to the electrical acceptor properties of the fluorine atom, the heminal chlorine atoms, in interaction with the  $\pi$ -system of the aromatic ring, created a non-covalent  $\pi$ -bond ( $3.351$  and  $3.401 \text{ \AA}$ ).



However, due to the electron acceptor properties of the fluorine atom, the chlorine hemal atoms in the neighboring molecule, interacting with the  $\pi$ -system of the aromatic nucleus, promoted the formation of a non-covalent bond ( $3.351$  v  $3.401 \text{ \AA}$ ) between the  $\cdots\pi$  intermolecular electron pair.

The main role of the halogen bonds  $C-Br\cdots Cl$ ,  $C-Cl\cdots Br$ ,  $C-H\cdots Cl$  in the formation of the crystal structure was determined by the Hirschfeld surface analysis. In addition, there is also the role of weak  $N\cdots H$  dipole interactions and  $\pi-\pi$  interactions in the formation of this structure.

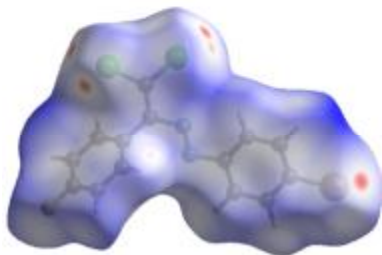
**Hirschfeld surface analysis 1-(4-Bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl)vinyl)diazene.** The Hirschfeld surface and fingerprints were taken on the basis of the crystallographic information file (CIF) using CrystalExplorer. The  $d_{norm}$  of the compounds obtained by us varies in the range of 0.2412-1.2981 Å, the formal index in the range of -1.0000 and 1.0000 Å, and the curvature in the range of -4.0000 and 4.0000 Å. In this crystal, the  $C-Br\cdots Cl$ ,  $C-Cl\cdots Br$ ,  $C-H\cdots Cl$  halogen bonds play a key role in the formation of the crystal structure. In addition, weak  $N\cdots H$  dipole-dipole interactions and  $p-p$  interactions also play a role in the formation of this structure.



$C-Br\cdots Cl$ ,  $C-Cl\cdots Br$ ,  $C-H\cdots Cl$  halogen bonds,  $N\cdots H$  interactions between the molecules in the crystal (Figure 3.3 in Mercury).

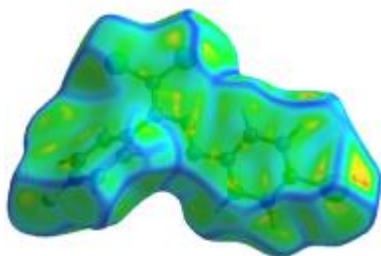
Although  $H\cdots H$ ,  $H\cdots C / C\cdots H$  interactions give a significant share (14%, 13.8%, respectively) to the Hirschfeld surface, according to Hirschfeld's surface analysis, the strong interactions in the crystal,  $Br\cdots Cl$  interactions. Indeed, in Hirschfeld's surface analysis, the surface area with close interactions is shown in red, the surface area with distant interactions is shown in blue, and the area between them is shown in white. Thus, the percentage of interatomic interactions in intermolecular interactions given to the Hirschfeld surface characterizes the magnitude of the interaction, not the proximity.

Note that dark red is used for strong interactions, light red for weak interactions, and blue indicates no interaction.



The  $d_{\text{norm}}$  of the compound Three-dimensional Hirschfeld surface in the range from -0.1010 a.u. to 1.4995 a.u.

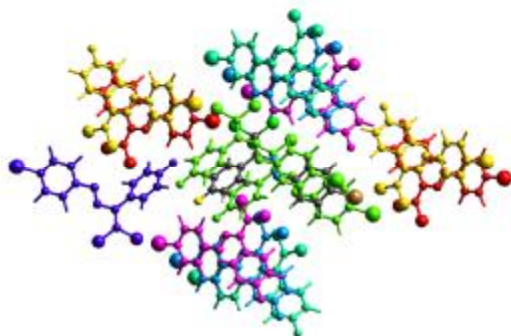
The curvature of the surface of the molecule is shown below. Where this surface is close to the plane, the curvature is small. The presence of a large plane area on both benzene nuclei, separated from the others by a blue line, indicates that they are in  $\pi \times \pi$  stacking interactions of other molecules in parallel with the corresponding benzene nuclei. The fact that the distance between one of the parallel nuclei of adjacent molecules, C4, and the other carbon C8, is 3.5 da, also corresponds to the characteristic-stacking interaction distance. This interaction ( $\text{C} \cdots \text{C}$ ) gives Hirschfeld an 8.6% share of the surface.



Molecular Hirschfeld surface: Curvedness

**Intermolecular interaction energies of 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl)diazene.** The total energy of interactions with a molecule in the neighborhood of a selected arbitrary molecule was calculated. Now let's present the calculated values of the energy of interaction of any selected molecule (Figure 4, black) with all the molecules in the neighborhood. Here, the selected molecule is relatively black, the other molecules are each colored, and the energy values corresponding to the colors in the table also show the full energy of the intermolecular interaction between the selected (black) molecule and that colored molecule:





The molecules around the selected (black) molecule are shown in different colors.

HF/3-21G

	N	Symmetry operation	R	E_ele	E_pol	E_dis	E_exc	E_full
	0	-x, y+1/2, -z+1/2	12.69	-3.6	-0.3	-8.7	10.6	-3.1
	0	-x, y+1/2, -z+1/2	12.69	-2.2	-0.1	-5.9	7.0	-1.9
	0	x, y, z	3.91	-11.7	-3.1	-88.8	54.3	-49.9
	0	x, -y+1/2, z+1/2	8.72	-4.0	-0.7	-11.1	8.1	-8.0
	0	x, -y+1/2, z+1/2	7.54	-9.0	-0.9	-23.5	17.4	-16.9
	0	-x, -y, -z	14.72	-5.5	-0.8	-7.8	2.2	-11.3
	0	x, -y+1/2, z+1/2	8.27	-2.0	-0.9	-11.6	2.5	-11.0

The interaction energies (kJ/mol) between the corresponding black molecule with molecules of a different color were calculated on the HF/3-21G model using the Crystal Explorer program.

Here R is the distance between the centers of the two molecules (Å). The center of a molecule is the center of the coordinates of the atoms of that molecule.

Hirfeld's surface analysis revealed that the C–Br···Cl, C–Cl···Br, C–H···Cl halogen bonds in this crystal played a key role in the formation of the crystal structure. In addition, weak N···H dipole-dipole interactions and p–p interactions were also found to play a role in the formation of this structure. The energy of intermolecular interactions was also calculated.

## RESULTS

1. The presence of an intermolecular non-covalent Cl···Cl bond

in the crystal structure of diazabutadienes synthesized under the conditions of catalytic olefination of benzoic aldehyde with phenylhydrazine was determined by X-ray diffraction analysis. Study of the antimicrobial properties of the synthesized (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene, this compound was found to have an effective effect against bacteria such as *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Candida albicans*.

2. From the reaction of the synthesized (E)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene derivatives with sodium azide, physiologically active 4-azido-2,5-diaryl-2H-1,2,3-triazoles in one step.

3. 1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl) diazene combining in its molecule atoms of chlorine, fluorine and bromine was synthesized and used as a model in a comparative study of non-covalent bonds of XRD studies, and it was determined that Br $\cdots$ Cl bonds relatively prevail over other bonds in the formation of the crystal.

4. Derivatives of bis-4,4-dichloro-1,2-diazabuta-1,3-diene were synthesized from various bis-phenylhydrazones of aromatic dialdehydes, the stereochemical properties of the reaction were studied by NMR and XRD, and it was determined that all reactions were observed mainly with the receipt of the E-isomer.

5. And in the case of 2,3,5,6-tetrafluoroterephthalic aldehyde, the presence of intermolecular and intramolecular (Cl $\cdots$ F, F $\cdots$ H, Cl $\cdots$  $\pi$ ) non-covalent bonds in the synthesized compounds was determined as a result of studies by XRD method.

6. The use of the corresponding bis-(4-((E)-(2,2-dichloro-1-(4-substituted phenyl) vinyl) diazenyl) phenyl) methanes synthesized on the basis of bis (4-hydrazinophenyl) methane was studied as azo dyes. In compounds of this type, the predominance of E isomers is formed due to intramolecular tetrahedral N $\cdots$ Cl and intermolecular hydrogen, halogen and chalcogen bonds.

7. Using the Hirfeld analysis method, it was found that the halogen bonds C–Br $\cdots$ Cl, C–Cl $\cdots$ Br, C–H $\cdots$ Cl in this crystal play the main role in the formation of the crystal structure. In addition, the effect of N $\cdots$ H dipole-dipole interactions and  $\pi$ – $\pi$  interactions in the formation of this structure was also discovered. The interaction energy between

molecules was also calculated.

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