New Materials, Compounds and Applications
Vol.5, No.3, 2021, pp.219-226

SYNTHESIS OF NEW DERIVATIVES OF POLYFUNCTIONAL DICHLORODIAZADIENES

Sevinc H. Mukhtarova[1,2*]

[1]Baku State University, Baku, Azerbaijan
[2]Azerbaijan Technical University, Baku, Azerbaijan

Abstract. In previous studies, dichlorodiazadiene dyes were synthesized based on the reaction of phenylhydrazones with CCl_4 obtained from the reaction of p-N, N-dimethylbenzaldehyde with 4-halogen (F, CI, Br) phenylhydrazines, and Hishfeld surface analyzes were studied. By continuing these studies, the corresponding dichlorodiazadienes were synthesized from hydrazones with two chlorine atoms (in the 2,6; 2,4; and 3,4 positions) in the hydrazine fragment. This will give an opportunity to the studies of the Cl ··· Cl bond, which can be formed as a result of the different positions of chlorine atoms, as well as the comparative studies of the Hishfield Surface Analyzes as isotipe compounds. Synthesized dichlorodiazabutadienes are important compounds in organic synthesis due to its structural properties. This allows them to be used in many areas, such as polyfunctional compounds, as syntons suitable for the synthesis of new classes of compounds.

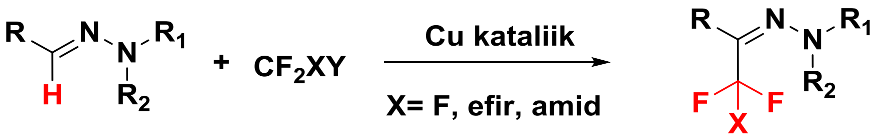
Keywords: *Phenylhydrazone, dichlorodiazadiene, diazodyes, non-covalent bonds, halogen bonds..*

Corresponding Author: *Sevinc H. Mukhtarova, Baku State University, Baku, Azerbaijan; Azerbaijan Technical University, Baku, Azerbaijan, email: mukhtarovasevinc@gmail.com*

Received: *28 September 2021;* ***Accepted:*** *22 November 2021;* ***Published:*** *7 December 2021.*

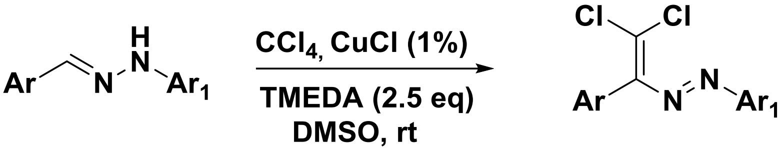
1. Introduction

Hydrazones are widely used in organic synthesis, supramolecular chemistry, obtaining complex compounds and dyes, and in the synthesis of many drugs in medical chemistry. The simple synthesis of hydrazones and their resistance to hydrolysis have led to their widespread use as suitable syntons. Thus, the multifunctional properties of the azometine group with a three-atom structure C = N-N allow its use in various fields. In particular, the reactions of hydrazones on the functionalization of the hydrogen atom C-H (sp^2) can be noted. There is a noteworthy point in the work done in this direction, which is the radical mechanism of functionalization of C-H (sp^2) bond in N, N-disubstitutedhydrazones (Prieto *et al.*, 2013; 2016; 2013; Pair *et al.*, 2013; Ke & Song, 2016). (Scheme 1).



Scheme 1. Functionalization of C-H (sp^2) bond in N, N-disubstituted hydrazones

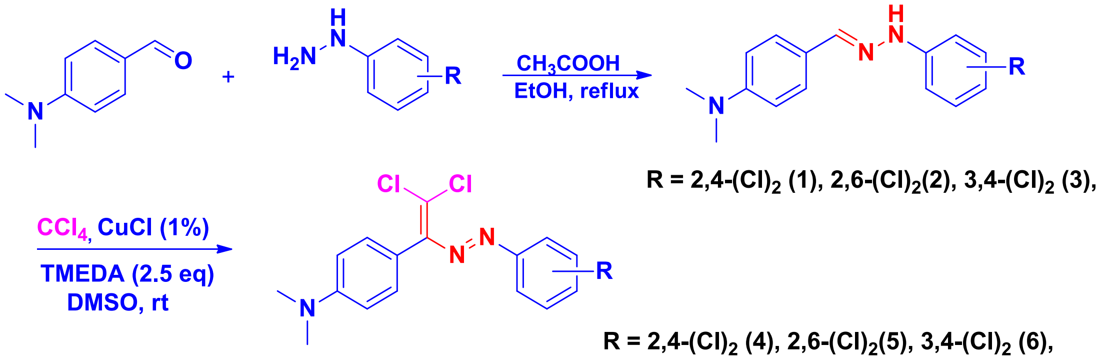
From the reaction of N-substituted hydrazones with CCl_4 in the presence of TMEDA in the catalytic content of CuCl, we have determined that the reaction of dichlorodiazabutadiene synthesis also follows a radical mechanism (Nenajdenko *et al.*, 2017). It should be noted that, in contrast to the functionalization of the C-H (sp^2) bond in N, N-disubstitutedhydrazones by radical mechanism, no reaction was observed in this reaction to obtain the H atom R radical substitution product, and the olefination reaction was determined (Scheme 2).



Scheme 2. General mechanism of catalytic olefination reaction

Dichlorodiazabutadienes, easily synthesized by this reaction, are important compounds in organic synthesis due to their structural properties. This allows them to be used in many areas, such as polyfunctional compounds (presence of heminal chlorine atoms, conjugated diene system, azo group), as syntones suitable for the synthesis of new classes of compounds (Aryl hydrazones of α-ketoether), azido 2H-1,2,3-triazoles, nitrogen containing heterocyclic compounds, etc.). Of particular note is our study of the role of non-covalent bonds (N···Cl, Cl···O, π···π and weak FЧЧЧπ halogen, CH···F hidrogen bonds) in the formation of single crystals of these compounds (Maharramov *et al.*, 2018; 2019; Shikhaliyev *et al.*, 2018; 2019a; 2019b; Nenajdenko *et al.*, 2020).

It should be noted that the nature and condition of the functional groups in the benzene rings not only give it a new design in the formation of crystals, but also create new applications in them. Taking into account the advantages listed above, we continued our research by synthesizing dichlorodiazabutadienes, containing dimethylamine group in the aldehyde fragment, and halogen atoms (F,CI, Br) in the hydrazine fragment in the para position and the same time Hirshfield Surface Analyze is investigated (Özkaraca *et al.*, 2020a; 2020b; Atioğlu *et al.*, 2020). As a follow-up to this reaction, dichlorodiazadienes were synthesized from hydrazones with two halogen atoms in the hydrazine fragment (Scheme 3).



Scheme 3. General scheme of dichlorodiazadiene obtaining

Keeping the amine group stable in the aldehyde fragment, and the inclusion of two chlorine atoms in the hydrazine fragment under different conditions, opens up new possibilities for studying the crystal design in the synthesized compounds. Thus, the new intra-molecular and intermolecular non-covalent bonds that may arise as a result of the different positions of chlorine atoms will lead to the study of the Cl ··· Cl bond as well as the comparative study of Hirschfeld's surface analysis as isotope compounds. In general, the main purpose of inserting two chlorine atoms into a hydrazine fragment under different conditions is to make it one of the most studied areas of halogen bonds at present.

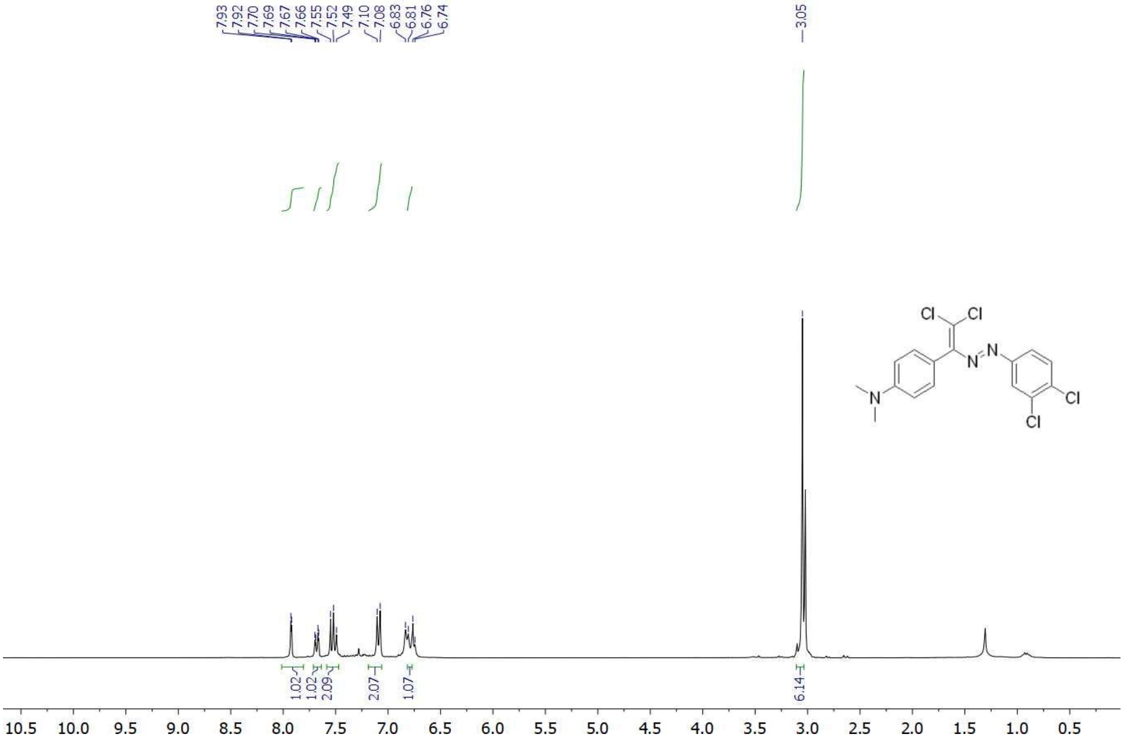


Fig. 1. ^{1}H NMR spectrum of compound 6

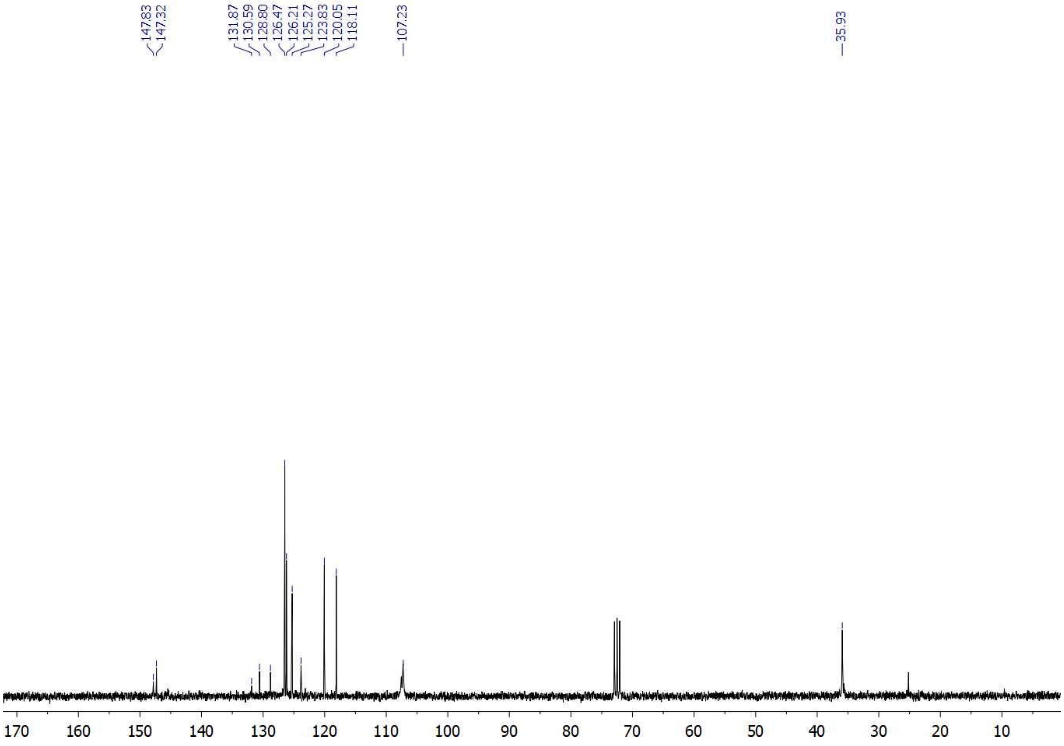


Fig. 2. ^{13}C NMR spectrum of compound 6

The structure of the compounds formed as a result of the reaction was confirmed by the NMR method. Lets take (E) -4- (2,2-dichloro-1 - ((3,4-dichloro-phenyl) diazenyl) vinyl) -N, N-dimethylaniline for example. Protons in the aromatic part resonate at δ7.92-6.91 at room temperature in the $CDCl_3$ (chloroform-D) solvent of the corresponding dichlorodiazabutadiene. In the 13C NMR spectrum of both compounds, all carbon atoms were found in the expected fields. The interpretation of the spectra clearly indicates the structure of the compounds. The known spectra are shown in Fig 1,2.

Due to the presence of chromophore diazo and halogen groups in the main products, the compound can be used as a dye, and the presence of halogen atoms suggests the presence of antimicrobial properties.

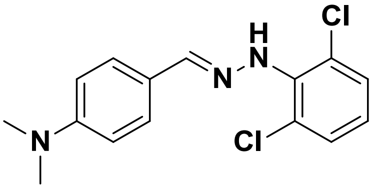
2. Experimental part

The NMR 1H and 13C spectra were recorded on a BrookerAvance 300 (operating frequency 300 MHz spectrometer in $CDCl_3$ and DMSO, respectively. $SiMe_4$ was used as the internal standard. TLC was carried out on Silufol board UT-254, and acidified $KMnO_4$ solution and UV lamp beams were used to clearly see the formed spots. Column chromatography was performed on Merck silicagel (63-200).

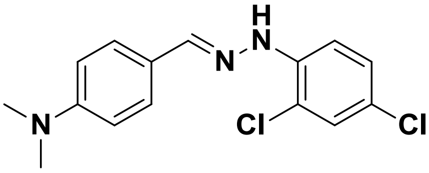
General methods of synthesis of hydrazones:

Ethanol (20-50 ml) and 0.820 g of CH_3COONa (10 mmol) are added to the phenylhydrazine added to the three-necked flask. The flask is connected to the counter-refrigerator, dropper funnel and thermometer. 5 mmol of aldehyde is added through the dropper funnel and the reaction mixture is stirred and heated. When the temperature reaches 78°C, the mixture is boiled for 5-10 minutes. The reaction mixture is then cooled to room temperature and 50 ml of water is added. With intensive stirring, the temperature is brought back to 60°C and the heating is stopped. The reaction mixture cooled to room temperature is filtered. If necessary, the residue of the product is washed with water. The obtained hydrazoneis dried at room temperature (15-20 hours). The NMR 1H and 13C spectra are consistent with the literature indicators.

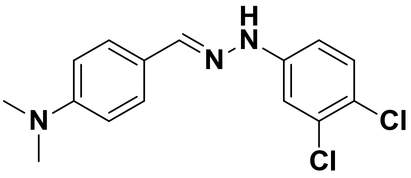
Substance 1. (E)-4-((2-(2,4-dichlorophenyl) hydrazone) methyl) -N, N-dimethylaniline: White solid (66%); mp 170 ° C. Analytically calculated $C_{15}H_{15}Cl_2N_3$ (M = 307.20),), ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.65 (s, 1H), 8.18 (s, 1H), 7.49 (dd, J = 8.8, 3.1 Hz, 3H), 7.42 (d, J = 2.2 Hz, 1H), 7.27 (dd, J = 8.9, 2.1 Hz, 1H), 6.73 (d, J = 8.7 Hz, 2H), 2.95 (s, 6H). ^{13}C NMR (75 MHz, DMSO) δ 146.63, 138.26, 136.88, 124.29, 123.84, 123.28, 118.67, 117.03, 112.00, 110.43, 107.85, 35.74.



Substance 2. (E)-4-((2-(2,6-dichlorophenyl) hydrazone) methyl) -N, N-dimethylaniline: White solid (67%); mp 115 °C. Analytically calculated$C_{15}H_{15}Cl_2N_3$(M = 307.20), ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.95 (s, 1H), 7.43 (d, J = 3.3 Hz, 2H), 7.40 (d, J = 3.9 Hz, 2H), 7.01 (t, J = 8.0 Hz, 1H), 6.70 (d, J = 8.8 Hz, 2H), 2.92 (s, 6H).^{13}C NMR (75 MHz, DMSO) δ 146.45, 137.03, 134.58, 125.16, 122.89, 122.00, 119.50, 118.97, 107.87, 35.77.



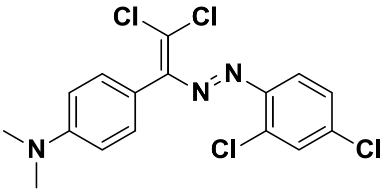
Substance 3. (E)-4-((2-(3,4-dichlorophenyl) hydrazone) methyl) -N, N-dimethylaniline: White solid (92%); mp 200 °C. Analytically calculated$C_{15}H_{15}$ Cl_2 N_3(M = 307.20), ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.28 (s, 1H), 7.79 (s, 1H), 7.49 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.7 Hz, 1H), 7.19 (s, 1H), 6.93 (d, J = 8.5 Hz, 1H), 6.72 (d, J = 8.6 Hz, 2H), 2.94 (s, 6H).^{13}C NMR (75 MHz, DMSO) δ 146.49, 141. 69, 135.80, 127.38, 126.66, 123.13, 118.72, 114.22, 108.20, 107.86, 107.79, 35.75.



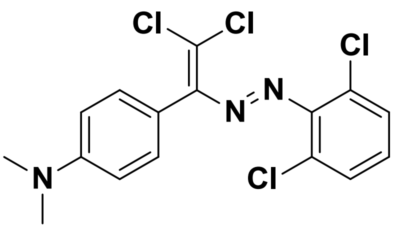
General method of synthesis of (E) -4- (2,2-dichloro-1 - ((dichlorophenyl) diazenyl) vinyl)-N, N-dimethylanilines

To the flask add 1 mmol starting hydrazone, 10-12 ml of DMSO, then (290 mg; 1.25 mol / eq) TMEDA. Then CuCl (6 mg; 3 mol%) is added, and finally CCl4 (4-5 mol / eq; 1.5 g). The magnetic mixer is activated. We check the reaction with TLC. The reaction usually takes 1.5-3 hours. The reaction mixture is transferred to the separator funnel. Add 50-60 ml of water. Extracted with methylene chloride (3 * 15 ml). The organic phase (3 * 50 ml) is washed with water and then with saturated NaCl (1 * 50 ml) solution. It is dried with Na_2SO_4 ($MgSO_4$), filtered and dichloromethane is removed by a rotor evaporator in a vacuum. The residue (eluent dichloromethane / hexane 1: 5) is re-cleaned by column chromatography. The fractions, which are the main reaction products separated by TLC, were collected and re-evaporated in the rotor and the yield was calculated.

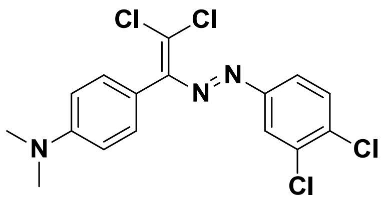
Substance 4. (E)-4-(2,2-dichloro-1-((2,4-dichlorophenyl) diazenyl)vinyl)-N,N-dimethylaniline. Red crystalline substance (45%), mp=140-142^0, Analytically calculated $C_{16}H_{13}Cl_4N_3$(M = 389,10),^{1}H NMR (300 MHz, Chloroform-d) δ 7.61 – 7.46 (m, 3H), 7.28 (s, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.01 (d, J = 8.5 Hz, 1H), 6.77 (s, 1H), 3.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 127.03, 125.78, 125.47, 125.39, 123.46, 123.39, 123.14, 113.96, 113.94, 111.32, 111.29, 25.13.



Substance 5. (E)-4-(2,2-dichloro-1-((2,6-dichlorophenyl) diazenyl)vinyl)-N,N-dimethylaniline. Red crystalline substance (40%), mp=140-142^0, Analytically calculated $C_{16}H_{13}Cl_4N_3$ (M = 389,10). ^{1}H NMR (300 MHz, Chloroform-d) δ 7.49 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.2 Hz, 1H), 7.16 (dd, J = 15.3, 8.1 Hz, 1H), 6.73 (q, J = 8.7 Hz, 3H), 3.01 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.73, 126.53, 125.21, 124.31, 123.86, 108.96, 107.09, 106.77, 106.26, 105.57, 35.59.



Substance 6. (E)-4-(2,2-dichloro-1-((3,4-dichlorophenyl) diazenyl)vinyl)-N,N-dimethylaniline. Red crystalline substance(55 %), mp=140-142^0, Analytically calculated $C_{16}H_{13}Cl_4N_3$(M = 389,10),^{1}H NMR (300 MHz, Chloroform-d) δ 7.92 (d, J = 2.1 Hz, 1H), 7.68 (dd, J = 8.5, 2.1 Hz, 1H), 7.58 – 7.47 (m, 2H), 7.09 (d, J = 8.7 Hz, 2H), 6.81 (s, 1H), 3.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.83, 147.32, 131.87, 130.59, 128.80, 126.47, 126.21, 125.27, 123.83, 120.05, 118.11, 107.23, 35.93.



Acknowledgement

This work was performed under the support of the Science Development Foundation under the President of the Republic of Azerbaijan (grant no. EIF-BGM-4-RFTF-1/2017-21/13/4).

References

Atioğlu, Z., Akkurt, M., Shikhaliyev, N.Q., Mukhtarova, S.H., Suleymanova, G.T., & Toze, F.A. (2020). Crystal structure and Hirshfeld surface analysis of 4-{2, 2-dichloro-1-[(E)-(4-chlorophenyl) diazenyl] ethenyl}-N, N-dimethylaniline. *Acta Crystallographica Section E: Crystallographic Communications*, *76*(7), 1033-1037.

Ke, M., Song, Q. (2016). Copper-Catalyzed C (sp^2)–H Difluoroalkylation of Aldehyde Derived Hydrazones with Diboron as Reductant. *The Journal of Organic Chemistry*, *81*(9), 3654-3664.

Maharramov, A.M., Shixaliyev, N.Q., Gurbanov, A.V., Mahmudov, K.T., Nenajdenko, V.G., Pombeiro, A.J., & Kopylovich, M.N. (2016). Halogen bonding in the synthesis and design of coordination and organometallic compounds. In *Non-Covalent Interactions in the Synthesis and Design of New Compounds*, 145-162.

Maharramov, A.M., Shikhaliyev, N.Q., Suleymanova, G.T., Gurbanov, A.V., Babayeva, G.V., Mammadova, G.Z., ... & Pombeiro, A.J. (2018). Pnicogen, halogen and hydrogen bonds in (E)-1-(2, 2-dichloro-1-(2-nitrophenyl) vinyl)-2-(para-substituted phenyl)-diazenes. *Dyes and Pigments*, *159*, 135-141.

Nenajdenko, V.G., Shastin, A.V., Gorbachev, V.M., Shorunov, S.V., Muzalevskiy, V.M., Lukianova, A.I., ... & Khrustalev, V.N. (2017). Copper-Catalyzed Transformation of Hydrazones into Halogenated Azabutadienes, Versatile Building Blocks for Organic Synthesis. *ACS Catalysis*, *7*(1), 205-209.

Nenajdenko, V.G., Shikhaliyev, N.G., Maharramov, A.M., Bagirova, K.N., Suleymanova, G.T., Novikov, A.S., ... & Tskhovrebov, A.G. (2020). Halogenated diazabutadiene dyes: Synthesis, structures, supramolecular features, and theoretical studies. *Molecules*, *25*(21), 5013.

Nenajdenko, V.G., Maharramov, A.M., Shıkhaliyev, N.G., Suleymanova, G.T., Gurbanov, A.V., Babayeva, G.V., Garazadeh, K.A., & Ahmedova, N.E.. (2019). Synthesis and structural study of dichlorodiazadienes derived from para-nitro benzaldehyde. *New Materials, Compounds and Applications*, *3*(3), 135-141.

Özkaraca, K., Akkurt, M., Shikhaliyev, N.Q., Askerova, U.F., Suleymanova, G.T., Shikhaliyeva, I.M., & Bhattarai, A. (2020a). Crystal structure and Hirshfeld surface analysis of 4-{2, 2-dichloro-1-[(E)-(4-fluorophenyl) diazenyl] ethenyl}-N, N-dimethylaniline. *Acta Crystallographica Section E: Crystallographic Communications*, *76*(6), 811-815.

Özkaraca, K., Akkurt, M., Shikhaliyev, N. Q., Askerova, U. F., Suleymanova, G. T., Mammadova, G. Z., & Mlowe, S. (2020b). Crystal structure and Hirshfeld surface analysis of 4-{2, 2-dichloro-1-[(E)-2-(4-methylphenyl) diazen-1-yl] ethenyl}-N, N-dimethylaniline. *Acta Crystallographica Section E: Crystallographic Communications*, *76*(7), 1122-1125.

Pair, E., Monteiro, N., Bouyssi, D., & Baudoin, O. (2013). Copper‐Catalyzed Trifluoromethylation of N, N‐Dialkylhydrazones. *Angewandte Chemie International Edition*, *52*(20), 5346-5349.

Prieto, A., Landart, M., Baudoin, O., Monteiro, N., & Bouyssi, D. (2015). Copper‐Catalyzed Trifluoromethylation of Aliphatic N‐Arylhydrazones: A Concise Synthetic Entry to 2‐Trifluoromethylindoles from Simple Aldehydes. *Advanced Synthesis & Catalysis*, *357*(13), 2939-2943.

Prieto, A., Melot, R., Bouyssi, D., & Monteiro, N. (2016). C–H Difluoroalkylation of Aldehyde Hydrazones with Functionalized Difluoromethyl Bromides under Copper Catalysis. *ACS Catalysis*, *6*(2), 1093-1096.

Shastin, A.V., Tsyrenova, B.D., Sergeev, P.G., Roznyatovsky, V.A., Smolyar, I.V., Khrustalev, V.N., & Nenajdenko, V.G. (2018). Synthesis of a New Family of 1, 1-Diazidoethenes: One-Pot Construction of 4-Azido-1, 2, 3-triazoles via Nitrene Cyclization. *Organic Letters*, *20*(24), 7803-7806.

Shikhaliyev, N.G., Maharramov, A.M., Suleymanova, G.T., Babazade, A.A., Nenajdenko, V.G., Khrustalev, V.N., Novikov, A.S., & Tskhovrebov, A.G.. (2021). Arylhydrazones of α-ketoestersviamethanolysis of dichlorodiazabutadienes: synthesis and structuralstudy. *Electronic Supplementary Materials Mendeleev Commun*., 31, 677–679.

Shikhaliyev, N.G., Maharramov, A.M., Suleymanova, G.T., Babayeva, G.V., Mammadova, G.Z., Shikhaliyeva, I.M., ... & Nenajdenko, V.G. (2021). Halogen-bonding in 3-nitrobenzaldehyde-derived dichlorodiazadienes. *Organic Chemistry*, (part iii).

Shikhaliyev, N. Q., Kuznetsov, M. L., Maharramov, A. M., Gurbanov, A. V., Ahmadova, N. E., Nenajdenko, V. G., ... & Pombeiro, A. J. (2019a). Noncovalent interactions in the design of bis-azo dyes. *Cryst. Eng. Comm.*, *21*(34), 5032-5038.

Shikhaliyev, N.Q., Ahmadova, N.E., Gurbanov, A.V., Maharramov, A.M., Mammadova, G.Z., Nenajdenko, V.G., ... & Pombeiro, A.J. (2018). Tetrel, halogen and hydrogen bonds in bis (4-((E)-(2, 2-dichloro-1-(4-substitutedphenyl) vinyl) diazenyl) phenyl) methane dyes. *Dyes and Pigments*, *150*, 377-381.

Shikhaliyev, N. G., Suleymanova, G. T., İsrayilova, A. A., Ganbarov, K. G., Babayeva, G. V., Garazadeh, K. A., ... & Nenajdenko, V. G. (2019b). Synthesis, characterization and antibacterial studies of dichlorodiazadienes. *Organic Chemistry*, (part vi), 64-73.

Tsyrenova, B.D., Khrustalev, V.N., & Nenajdenko, V.G. (2021). Synthesis of blue light emitting heterocycles via cyclization of 2-pyridine derived 4-azido-r1, 2, 3-triazoles. *Organic & Biomolecular Chemistry*, *19*(37), 8140-8152.

Tsyrenova, B., Khrustalev, V., & Nenajdenko, V. (2020). 2 H-Bis-1, 2, 3-triazolo-isoquinoline: Design, Synthesis, and Photophysical Study. *The Journal of Organic Chemistry*, *85*(11), 7024-7035.