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SYNTHESIS OF HALOGENATED DIAZABUTADIEN DYES BASED ON 4-HALOGEN BENZALDEHYDE

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Abstract. Reactions between 4-halogenbenzaldehyde and corresponding phenyl hydrazine in a presence of catalytic olefination have resulted synthesizing proper phenylhydrazones, at the end of reaction of derivatives with CCl_4, halogenated diazabutadien dyes has synthesized. Existing different halogen atoms in each substance, conjugated systems and azo groups, result in inter- and intramolecular non-covalent bonds.

Keywords: *Catalytic olefination reaction, phenylhydrazon, diazabutadiene, non-covalent bond.*

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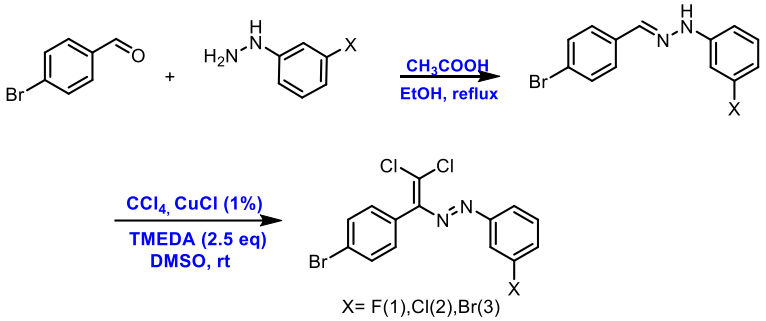
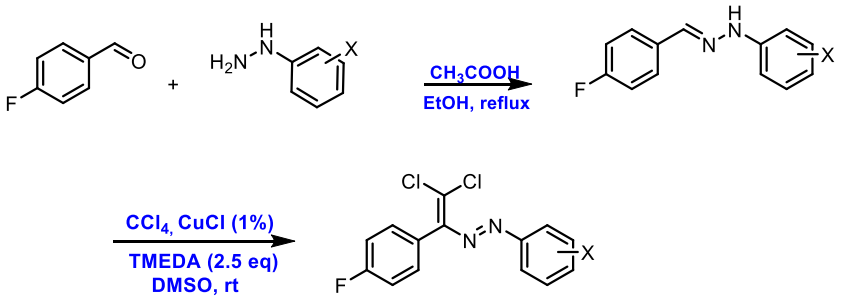
1. Introduction

Reactions between aromatic aldehydes and different substituted phenylhydrazines in a presence of catalytic olefination have resulted synthesizing corresponding N-substituted phenylhydrazones and dihalogendiazadiens have synthesized in a reaction between reaction product and polyhalogenalkanes (Maharramov *et al.*, 2016; 2017a,b; 2018a,b,c; Shikhaliyev *et al.*, 2016a,b; Nenajdenko *et al.*, 2019). According to the nature of polyhalogen alkanes, for example during the reaction with CBr_4, vinylbenzole was also synthesized with diens, thus, effect of the nature of halogen atoms on the direction of the reaction was found. At the same time, properties of these compounds as diaza dyes and physiological active substances were studied (Shikhaliyev *et al.*, 2018; 2019a,b; Maharramov *et al.*, 2018d). We can add that, polyhalogenated substances solve well in organic solvents, so this property makes them important as suitable syntons in organic synthesis. Synthesis of corresponding dichlorodiazadiens which keep halogen atoms in hydrazine and aldehyde fragment is important for crystallochemistry (Abdullayeva *et al.*, 2019; Gajar *et al.*, 2020; Nenajdenko *et al.*, 2020). So, these compounds can be used as a model for researching non-covalent halogen-halogen bondings. That's why, from the reaction of corresponding phenylhydrazones and CCl4, which were synthesized from 4-bromo benzaldehyde and 3-halogenphnylhydrazines, corresponding (E)-1-(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(3-halogenphenyl) diazenes have synthesized (Scheme 1).

Hydrazones have synthesized in analogical way and the structure of dichlorodiazadiens were proved by NMR method (Soubhye *et al.*, 2017). Considering the effect of halogen-halogen bondings on crystal design, corresponding reactions of 4-floro benzaldehyde have studied.



Scheme 1. General reaction of obtaining of (E)-1-(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(3-halogenephenyl)diazenes



The structure of synthesized compounds was proved by NMR method. Also, molecular structure of (E)-1-(2,4-dichlorophenyl)-2-(4-florobenzydilene)hydrazine was learnt by X-ray Structural Analysis and the effect of intermolecular halogen-halogen non-covalent interactions on crystal packing have determined. In a compound 8, F atom in aldehyde fragment makes halogen-halogen non-covalent interactions with heminal chloro atom of other molecule (3.018Å) and chloro atom in hydrazine fragment (3.114Å) (Fig.1).

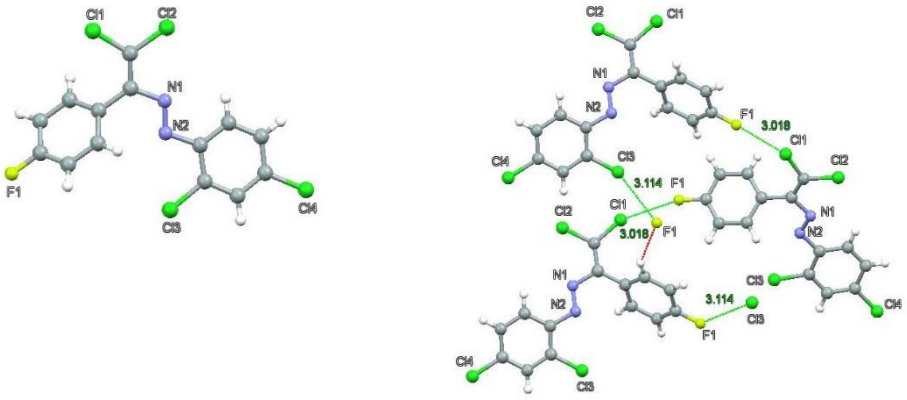


Fig.1. Molecular structure of (E)-1-(2,4-dichlorophenyl)-2-(4-florobenzydilene)hydrazine and halogen-halogen (F...Cl) non-covalent interactions were showed by short lines

So, halogenated diazabutadiene dyes based on 4-F and 4-Br benzaldehyde have synthesized and non-covalent halogen-halogen interactions in crystal packing were determined by X-ray Structural Analysis. Excisting F, Cl and Br, Cl in these compounds at the same time, may allow to study them as new group compounds to learn halogen-halogen interactions.

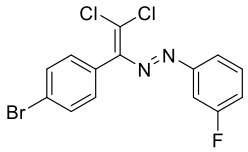
2. Experimental Part

The NMR ^{1}H and ^{13}C spectra were obtained by the BrukerAvance 300 (working frequency 300 and 75 MHz solvents $CDCl_3$ and $DMSOd_6$).TMS was used as an standard, and 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 silica gel (Merck 63-200).

The general preparation method of dichlorodiazadienes

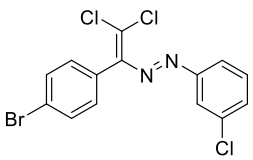
1 Mmol of starting (E) - (2,2-dichloro-1-phenylvinyl) diazenyl) phenyl) methanes is added to the flack, then 10-12 ml of DMSO, and then (290 mg; 1.25 mol / eq) TMEDA are added.Further catalyst CuCl (6 mg; 3 mol%) is added. Finally, CCl4 (4-5 mol / eq., 1.5 g) is added. The reaction mixture was stirred. Typically, the reaction goes in 1.5-3 hours. at the end of reaction 50-60 ml of waterisadded. Then the product ofreaction is extracted with methylene chloride (3 * 15 ml). After washing with water (3 * 50 ml) organic phase washed once with saturated NaCl solution (1 * 50 ml). Dried with Na_2SO_4 ($MgSO_4$), filtered and dichloromethane was removed by rotor evaporation in the vacuum. The residue (eluent is dixloromethane / hexane 1: 5) is purificated by column chromatography method. Fractions containing the main reaction product identified by TLC

Substance 1: (E)-1-(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(3-fluorophenyl)diazene –



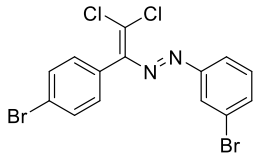
It is obtained reaction from (E)-1-(4-bromobenzyli-dene)-2-(3-fluorophenyl) hydrazine with CCl_4. yield 46%, red solid substance, Tmelt.=116°C, analitically calculated $C_{14}H_8BrCl_2FN_2$ (M=371.92), ^{1}H NMR (300 MHz, $CDCl_3$) δ7.48 (ddt, *J* = 12.9, 8.3, 1.8 Hz, 2H), 7.44 – 7.35 (m, 1H), 7.23 – 7.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.88, 161.86, 150.70, 150.64, 147.76, 134.98, 134.11, 131.92, 131.82, 123.58, 123.52, 123.46, 119.08, 119.06, 115.31, 115.15, 110.68, 110.52.

Substance 2: (E)-1-(1-(4-bromophenyl)-2,2-dichlorovinyl)-2-(3-chlorophenyl)diazene-



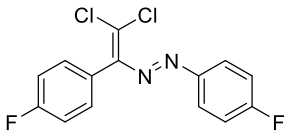
It is obtained reaction from (E)-1-(4-bromobenzilidene) -2-(3-chlorophenyl)hydrazin with CCl_4 . yield 40%, red solid substance, Tmelt.=75-76°C, analitically calculated $C_{14}H_8BrCl_3N_2$ (M=387.89), ^{1}H NMR (300 MHz, $CDCl_3$) δ7.71 – 7.61 (m, 2H), 7.57 (dt, *J* = 7.5, 2.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ150.54, 147.74, 135.08, 134.93, 134.14, 131.95, 131.84, 130.64, 130.06, 123.40, 122.15, 121.57.

Substance 3: (E)-1-(3-bromophenyl)-2-(1-(4-bromophenyl)-2,2-dichloro-vinyl)diazene-



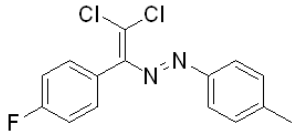
It is obtained reaction from (E)-1-(4-bromobenzilidene)-2-(3-bromophenyl)hydrazin with CCl_4. yield 39%, red solid substance, $T_{melt.}$=108-109°C, analitically calculated $C_{14}H_8Br_2Cl_2N_2$ (M=431.84), ^1H NMR (300 MHz, $CDCl_3$) δ7.88 (t, *J* = 2.0 Hz, 1H), 7.64 (dp, *J* = 7.5, 2.0 Hz, 2H), 7.49 – 7.40 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.12 (m, 2H). ^{13}C NMR (75 MHz, CDCl 3) δ 150.85, 147.71, 134.90, 134.12, 131.90, 131.80, 130.21, 129.00, 124.77, 123.43, 122.47, 120.15

Substance 4: (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(4-fluorophenyl)diazene-



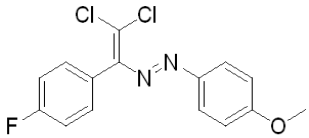
It is obtained reaction from (E)-1-(4-florobenzydilene)-2-(4-florophenyl)hydrazine with CCl_4.Yield 31%, red solid substance, $T_{melt.}$=95°C, analitically calculated $C_{14}H_8CI_2F_2N_2$, (M=313.12). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.88 – 7.78 (m, 2H, arom), 7.24 – 7.07 (m, 6H, arom). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.58, 132.46, 131.98, 131.87, 125.40, 125.28, 116.27, 116.07, 115.96, 115.72, 115.53, 115.43, 115.25, 115.09.

Substance 5: (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(p-tolyl)diazene-



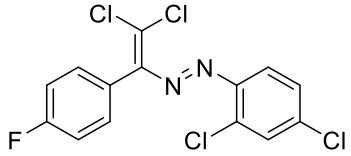
It is obtained reaction from (E)-1-(4-florobenzydilene)-2-(p-toluol)hydrazinewith CCl_4.Yield 40%, red solid substance, $T_{melt.}$=86°C, analitically calculated $C_{15}H_{11}CI_2FN_2$(M=309.16). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H, arom), 7.25 (s, 2H, arom), 7.22 – 7.10 (m, 4H, arom), 2.42 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.41, 161.12, 151.38, 150.98, 142.51, 132.03, 131.92, 129.76, 128.45, 123.27, 115.46, 115.17, 21.60.

Substance 6: (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(4-methoxyphenyl)diazene –



It is obtained reaction from (E)-1-(4-florobenzydilene)-2-(4-metoxyphenyl)hydrazine with CCl_4.Yield 44%, red solid substance, $T_{melt.}$=65°C, analitically calculated $C_{15}H_{11}CI_2FN_2O$, (M=325.16). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.9 Hz, 2H, arom), 7.20 – 7.09 (m, 4H, arom), 6.95 (d, *J* = 8.9 Hz, 2H, arom), 3.88 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.92, 162.32, 152.05, 148.81, 131.89, 125.28, 115.41, 115.12, 114.21, 110.62, 101.23, 99.98, 55.61.

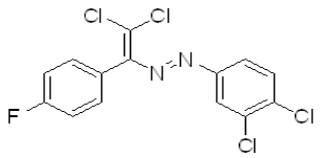
Substance 7: (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(2,4-dichlorophenyl)diazene-



It is obtained reaction from(E)-1-(2,4-dichlorophenyl)-2-(4-florobenzydilene)hydrazine with CCl_4.Yield 30%, red solid substance, $T_{melt.}$=72°C, analitically calculated $C_{14}H_{17}Cl_4FN_2$ (M=364.02), ^1H NMR (300 MHz, Chloroform-*d*) δ 7.83 – 7.58 (m, 1H, arom), 7.58 – 7.47

(m, 1H, arom), 7.46 – 7.31 (m, 1H, arom), 7.14 (ddt, *J* = 29.7, 21.0, 10.3 Hz, 4H, arom). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.83, 132.15, 132.04, 130.48, 129.17, 128.67, 128.08, 127.73, 118.33, 115.97, 115.74, 115.41, 115.12, 114.89.

Substance 8 : (E)-1-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-2-(3,4-dichlorophenyl)diazene-



It is obtained reaction from(E)-1-(3,4-dichlorophenyl)-2-(4-florobenzydilene)hydrazine with CCl_4.Yield 25%, red solid substance, Tmelt.=101°C, analitically calculated $C_{14}H_{17}Cl_4FN_2$ (M=364.02),^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.66 – 7.50 (m, 4H, arom), 7.49 – 7.34 (m, 2H, arom), 7.24 (d, *J* = 8.5 Hz, 1H, arom). ^{13}C NMR (75 MHz, $CDCl_3$)δ 164.60, 162.59, 148.98, 147.76, 134.98, 133.79, 133.76, 132.08, 131.84, 131.77, 131.43, 130.28, 129.88, 122.41, 116.02, 115.86.

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References

Abdullayeva, A.A., Ahmadova, N.E., Suleymanova, G.T., Ganbarova, J.G., Babayeva, G.V., Gurbanova, N.V., Shikhaliyev, N.G., Maharramov, A.M. (2019). Triazole synthesis based on dichlorodiazadienes. *Transactions of Pedagogical University. Series of Mathematical and Natural Sciences*, *67*(3), 58-66.

Gajar, A.M., Abdulov, M.S., Ibrahimova, Sh.A., Suleymanova, G.T., Babayeva, G.V., Shikhaliyev, N.G., Maharramov, A.M. (2020). Synthesis of Dichlorodiazabutadienes based on 4- methylbenzaldehyde. *Transactions of Pedagogical University. Series of Mathematical and Natural Sciences*, *68*(1), 39-47.

Maharramov, A.M., Ahmadova, N.E., Gajar, A.M., Askerova, U.F., Shikhaliyev, N.Q., Nenaydenko, V.G. (2017a). Synthesis and molecular structure of bis-dichlordiazabutadiene from bisphenylhydrazones of benzoic aldehyde derivatives. *Baku University News*, 2, 5-11.

Maharramov, A.M., Shikhaliyev, N.G., Suleymanova, G.T., Bagirova, Kh.N., Asgerova, U.F., Garazadeh, Kh.A., Babayeva, G.V., Ahmedova, N.E., Nenajdenko, V.G. (2018a). Synthesis of dihalogendiazadiene and farmazan derivatives in the catalytic olefinization reaction. *Journal of Low Dimensional Systems, 2*(2), 24-29.

Maharramov, A.M., Shikhaliev, N.G., & Gurbanov, A.V. (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., Suleymanova, G.T., Babayeva, G.V., Ibragimova, Sh.A., Niyazova, A.A., Shikhaliev, N.G., Musayev, F.N., Nenaidenko, V.G. (2018b). Synthesis of compounds of dichlorodiazabutadiene structure from benzoic aldehyde and some of its derivatives based on the catalytic olefination reaction. *Chemical Problems*, 2, 230-238.

Maharramov, A.M., Shixaliyev, N.Q., Suleymanova, G.T., Gurbanov, A.V., Mammadova, G. Z., Nenajdenko, V.G., Zubkov, F.I., Mahmudov, K.T., Pombeiro, A.J.L. (2018c). Pnicogen, halogen and hydrogen bonds in (E)-1-(2,2-dichloro-1-(4-substitutedphenyl)vinyl)-2-(2nitrophenyl) diazenes. *Dyes and Pigments*, 159, 135-141.

Maharramov, A.M., Suleymanova, G.T., Garazadeh, Kh.A., Mammadova, N.A., Mamedov, I.G., Hasanova, U.A., Nenajdenko, V.G., Shikhaliev, N.G. (2018d). Synthesis and X-ray investigation of nitro, dichlorine derivatives of 1- (2,2-dichloro-1phenylvinyl) -2-phenyldiazene by catalytic olefination reaction. *Journal of Low Dimensional Systems, 2*(1), 37-44.

Maharramov, A.M., Askerova, U.F., Akhmedova, N.E., Mukhtarova, S.Kh., Garazadeh, Kh.A., Shikhaliev, N.G. (2017b). Synthesis and study of the antimicrobial activity of (E) -1- (2,2- dichloro- 1- phenylvinyl) -2- phenyl- diazene. *Journal of Low Dimensional Systems, 1*(1), 4-7.

Nenajdenko, V.G., Maharramov, A.M., Shıkhaliyev, N.G., Suleymanova, G.T., Gurbanov, A.V., Babayeva, G.V., Garazadeh, Kh.A., Ahmedova, N.E. (2019). Synthesıs and structural study of dıchlorodıazadıenes derıved from para-nıtro benzaldehyde. *New Materials, Compounds and Applications, 3*(3), 135-141.

Nenajdenko, V.G., Shikhaliyev, N.G., Maharramov, A.M., Bagirova, Kh., Suleymanova, G.T., Novikov, A.S., Khrustalev, V.N., Tskhovrebov, A.G. (2020). Halogenated Diazabutadiene Dyes: Synthesis, Structures, Supramolecular Features, and Theoretical Studies. *Molecules, 25*(21), 5013.

Shikhaliyev, N.Q., Ahmadova, N.E., Gurbanova, A.V., Maharramov, A.M., Mammadova, G.Z., Nenajdenko, V.G., Zubkov, F.I., Mahmudov, K.T., Pombeiro, A.J.L. (2018). Tetral, 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.Q., Gurbanova N.V., Ahmadova N.E., Mukhtarova S.H., Suleymanova G.T., Maharramov, A.M., Nenaydenko, V.Q. (2016a). Synthesis of dihalogendiazadiens from benzylidene -2-phenylhydrazine on the basis of catalytic olefination reaction. *Baku University News,* 3, 5-12.

Shikhaliyev, N.G., Gurbanova, N.V., Ahmedova, N.E., Muhtarova, S.H., Suleymanova, G.T., Maharramov, A.M., Nenaydenko, V.G. (2016b). Synthesis of dihalogendiazadienes, based on catalytic olefination reaction of benzylidene-2-phenylhydrazine. *Baku University News,* 3, 5-12.

Shikhaliyev, N.G., Maharramov, A.M., Suleymanova, G.T., Babayeva, G.V., Mammadova, G.Z., Shikhaliyeva, I.M., Babazade, A.A., Nenajdenko, V.G. (2021). Halogen bonding in (E)-1-(2,2-dichloro-1-(3-nitrophenyl)vinyl)-2-(para-substituted phenyl) diazene dyes. *Arkivoc,* iii, 67-75.

Shikhaliyev, N.G., Suleymanova, G.T., Israyilova, A.A. Ganbarov, Kh.G., Babayeva, G.V., Garazadeh, Kh.A., Mammadova, G.Z. (2019a). Synthesis, characterization and antibacterial studies of dichlorodiazadienes derivatives. *Arkivoc,* 6475-6482

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

Soubhye, J., Gelbcke, M., Antwerpen, P.G.V, Dufrasne, F.M.U, Boufadi, M.Y., Neve, J., Paul, F.G., Obinger, C., Boudjeltia, K.Z., Meyer, F. (2017). From dynamic combinatorial chemistry to in vivo evaluation of reversible and irreversible myeloperoxidase inhibitors. *ACS Medical Chemistry Letters, 8*(2), 206-210.