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SYNTHESIZE OF (E)-1-(4-HALOGENPHENYL)-2-(2,2-DİCHLORO-1-(4-FLUOROPHENYL)VİNYL)DIAZENES AND THEM X-RAY STRUCTURAL ANALYSIS

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Abstract. During last years, the experiments on the halogen-halogen non-covalent interactions which have a great role in synthesize, catalytic and crystal engineering are used widely. According to this, corresponding dichlorodiazenes have been synthesized in catalytic olefinization conditionon the basis of 4-fluoro benzoy aldehyde. F in aldehyde fragment and Cl and Br atoms in hydrazine fragment of synthesized dichlorodiazadienes have an important role in determination of halogen-halogen non-covalent interactions. Cl···Cl, Cl···Br non-covalent interactions have a role in making monocrystal of the title compound and these interactions are investigated by X-Ray Structural Analysis.

Keywords: *dichlorodiazadienes, non-covalent interactions, catalytic olefinization reaction.*

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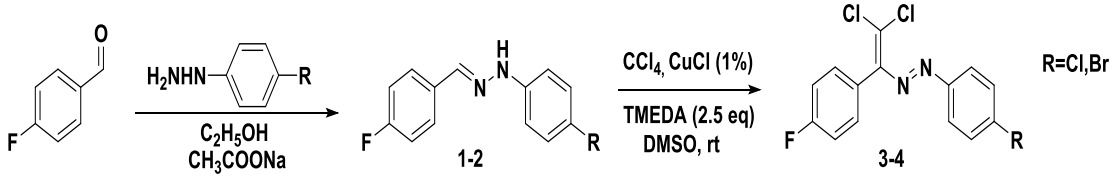
1. Introduction

Adding halogen atoms (F, Cl, Br) to the aldehyde and hydrazine fragments beforehand, results with the new non-covalent interactions, and this helps to investigate non-covalent interactions with it as a model. 4,4-dichloro-1,2-diazabuta-1,3-dien structures of N-substituted phenylhydrazones which have synthesized in catalytic olefinization condition, are important sintons in weak-organic synthesis. In these compounds non-covalent interactions were determined by X-Ray Structural Analysis Method (Nenajdenko *et al.*, 2017; Maharramov *et al.*, 2018, Maharramov *et al.*, 2018; Shikhaliyev *et al.*, 2018; Israyilova *et al.*, 2017; Maharramov *et al.*, 2017; Atioğlu *et al.*, 2019). Thus, we have synthesized dichlorodiazabutadienes which keep halogen group.



Scheme 1. Reaction of forming dichlorodiazabutadienes

The structure of the title compound was determined by X-Ray Structural Analysis Method (Picture 1).

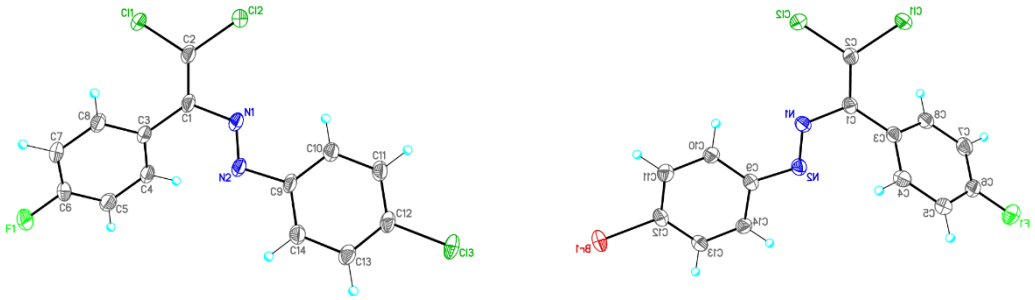


Figure 1. Molecular structures of (E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-(4-fluorophenyl) vinyl)diazene and (E)-1-(4-bromophenyl)-2-(2,2-dichloro-1-4-fluorophenyl)vinyl)diazene

Table 1. Chrystallographic and structural data of 3 and 4.

Formule	**$C_{14}H_8C_{l3}FN_2$**	**$C_{14}H_8BrCl_2FN_2$**
Mr	329.57	374.02
Sphere qroup	P 21/c	P 21/c
a, (Å)	3.8617(8)	3.9149(8)
b, (Å)	24.249(5)	24.549(5)
c, (Å)	14.724(3)	14.759(3)
α, ^{0}	90	90
β, ^{0}	94.30(3)	93.85(3)
γ, ^{0}	90	90
V, (Å^3)	1374.9(5)	1415.2(5)
ρ(Calc.),g/cm3	1.592	1.755
Z	4	4

Heminal Cl atoms in dichlorodiazenes, also halogen atoms (Cl, Br) in hydrazine fragment result with a non-covalent interactions between halogen-halogen atoms. So, in 3 Cl···Cl is [3.384 Å] and in 4 Cl···Br is [3,491 Å], that are smaller than accepted Van der Vaals radius.

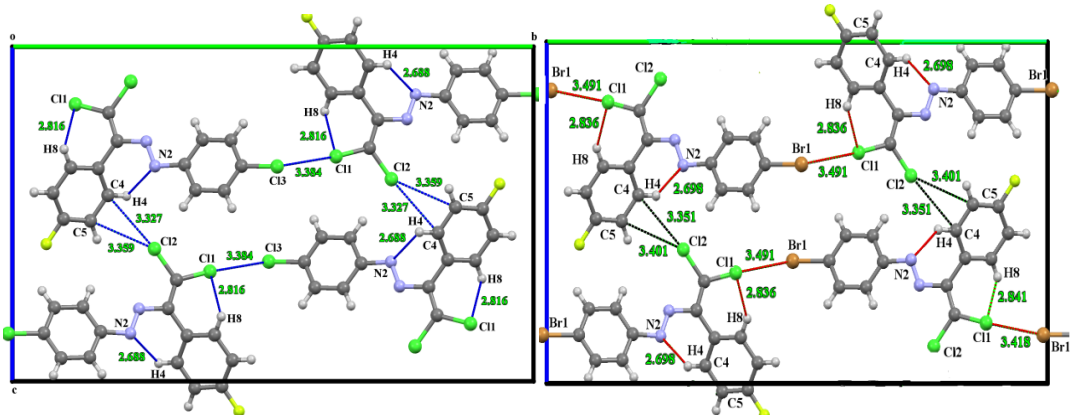


Figure 2. Non -covalent interactions in 3 and 4 are shown with short lines

Thus, adding halogen atoms (Cl, Br) to the title compound results with new non-covalent interactions (Pic.2), so this kind of compounds are used as azodyes (Shikhaliyev *et al.,* 2018; Maharramov *et al.,* 2018), also help to investigate non-covalent interactions as a model.

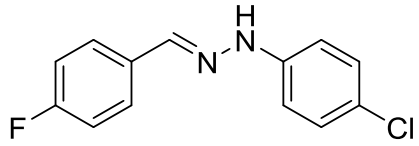
2. Experimental part

X-Ray Structural Analysis of 3 and 4 was carried out using of Bruker APEX II CCD diffractometer (T = 273 K, λMoKα-radiation, graphite monochromator, φ- and ω-scanned). The NMR ^{1}H and ^{13}C spectra were obtained by the Bruker Avance 300 (working frequency 300 and 75 MHz solvents $CDCl_3$ and $DMSOd_6$).TMS was used as a 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).

3. General methods of synthesing of hydrazones

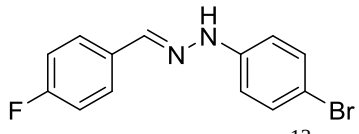
Ethanol (20-50 ml) and 0.820 g of CH_3COONa (10 mmol) are added to phenylhydrazine (5 mmol) in the tripodic tubular flack. Then 5mmol of aldehyde dropwise added and reaction mixture is stirred and heated. When the temperature reaches 78°C, the mixture is boiled for 5-10 minutes. Then, the reaction mixture is cooled to room temperature, 50 ml ofdistilled water is added to reaction mixture. Temperature reaches 60°C at intensive stirring. The cooled to room temperature reaction mixture is filtered. If necessary, the residue of the product is washed with distilled water. The resulting hydrazine is dried at ambient temperature (15-20 hours). The NMR 1H and 13C spectra are compatible with the literature.

Substance1:(E)-1-(4-chlorophenyl)-2-(4-fluorobenzilidene)hydrazine-$C_{13}H_{10}ClFN_2$



(248,68), yield 77%, white solid substance, Tmelt.=135-136°C, ^{1}H NMR (300 MHz, DMSO) δ7.05-7.08(d,2H,J=9.14Hz), 7.19(s,1H),7.23-7.25(d,3H,J=6.15Hz),7.68-7.72(m,2H), 7.87(s,1H),10.48(s,1H). ^{13}C NMR (75 MHz, DMSO)δ113.83, 115.94, 116.23, 122.39, 129.05, 128.16, 129.35, 132.61, 132.65, 136.63, 144.66, 160.81, 162.32, 164.06.

Substance2:(E)-1-(4-bromophenyl)-2-(4-fluorobenzilidene)hydrazine- $C_{13}H_{10}BrFN_2$

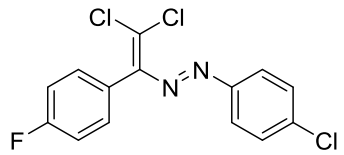


(293.13), yield 72 %, white solid substance, Tmelt.=130-132°C, ^{1}H NMR (300 MHz, DMSO-d_6) δ7.01-7.03(d,2H,J=6.04Hz), 7.19-7.25(t,2H,J=9.05Hz), 7.35-7.38(d,2H,J=9.12Hz), 7.68-7.73(m,2H), 7.87(s,1H),10.49(s,1H). ^{13}C NMR (75 MHz, DMSO)δ114.35, 115.94, 116.23, 128.07, 132.18, 132,63, 136,73, 145.03, 109.98.

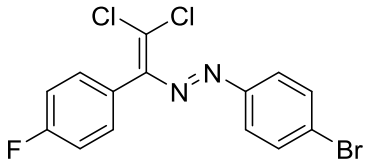
4. General methods of synthesizing ((2,2-dichloro-1-phenylvinyl)diazenile)phenyl_methan derivatives

1 Mmol of starting hydrazone is added to the flack, then 10-12 ml of DMSO, and then (290 mg; 1.25 mol/equiv) TMEDA are added. Further catalyst CuCl (6 mg; 3 mol%) is added. Finally, CCl4 (4-5 mol/eq.,1.5 g) is added. Typically, the reaction goes in 1.5-3 hours. At the end of the reaction 50-60 ml of water is added. Then, the product of reaction is extracted with methylene chloride (3x15 ml). After washing with water (3x50 ml) organic phase washed once with saturated NaCl solution (1x50 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.

Substance3:(E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1(4-fluorophenyl)vinyl)diazene- $C_{14}H_8Cl_3FN_2$ (329,58), yield 56%, red solid substance, Tmelt.=65-67°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ7.15-7.17(m,4H), 7.42-7.45(d,2H,J=9.21Hz), 7.73-7.75(d,2H, J=6.04Hz). ^{13}C NMR (75 MHz, $CDCl_3$)δ115.29, 115.58, 124.49, 127.46, 129.37, 130.43, 131.88, 131.99, 137.73, 151.13.



Substance4:(E)-1-(4-bromophenyl)-2-(2,2-dichloro-1(4-fluorophenyl)vinyl)diazene- $C_{14}H_8Cl_2FBrN_2$ (374.03), yield 58%, red solid substance,Tmelt.=67-65°C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.15 (d, 3H, J=3.12Hz), 7.17 (s,1H), 7.58-7.68 (m, 4H).^{13}C NMR (75 MHz, CDCl 3)δ115.29, 115.58, 124.67, 126.28, 131.87, 132.36, 151.49, 161.20, 162.32, 164.49.



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