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SYNTHESIS AND X-RAY STRUCTURAL ANALYSIS OF (E)-4-{2,2-DICHLORO-1-((PARA-HALOGENOPHENYL) DIAZENYL]VINYL}-N,N-DIMETYLANILINES

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Abstract. In a presence of catalytic olefination phenylhydrazones which have been obtained from the reaction of 4-halogen substituted phenyl hydrazines with p-N,N-dimetylbenzaldehyde form corresponding Eisomers of dichlorodiazadien dyes. This shows selectivity of the reaction, which also explains importance of non-covalent halogen bondings in crystal packing. These bondings were confirmed not only by X-ray Structural Analysis, but also Hirshfeld surface analysis. Synthesis of (E)-4-{2,2-dichloro-1-[(para-halogenophenyl)diazenyl]vinyl}-N,N-dimetylanilines are used as a model for exploring non-covalent interactions, which will be important compounds in the dye industry because of diaza group.

Keywords: *phenylhydrazone, dichlorodiazadien, diaza dyes, non-covalent interactions, halogen bondings.*

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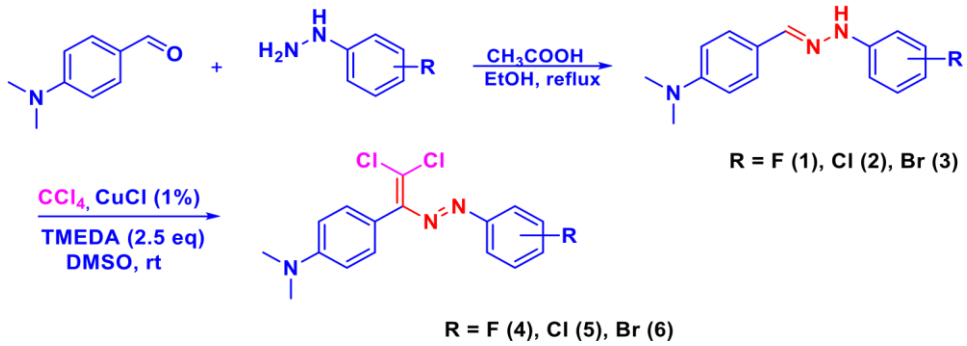
1. Introduction

In our previous research, phenyl hydrazones were synthesized from various functional substituted derivatives of benzyl aldehyde with corresponding phenyl hydrazines, then dichlorodiazabutadiens were prepared from the CuClcatalytic reaction with CCl4 in the presence of TMEDA (Maharramov *et al*., 2016; Shıkhaliyev *et al*., 2016a; Nenajdenko *et al*., 2017; Maharramov *et al*., 2018a,b,c). Synthesized compounds are important synthons in fine organic synthesis. So that, existingheminalchloro atoms, combined diene systems, azo groups make them valuable in medicine, dye industry and other fields (Shikhaliyev *et al.*, 2019; Suleymanova, 2018, 2019; Nenajdenko *et al*., 2019). Thus, these studies applied to aldehydes and found positive results (Shıkhaliyev *et al.*, 2016b, 2018, 2021; Ahmadova, 2019a, 2019b; Abdullayeva *et al.*, 2019; Gajar *et al.*, 2020).

We can add that, existing chromophorediaza groups in synthesized compounds makes studies of their dye properties convenient. Also, existing halogen atoms in compounds helps to investigate noncovalent interactions, intermolecular Hirshfeld surface analysis, and to calculate percentage of these interactions with "finger prints" (Atioğlu *et al*., 2019, 2020a,b; Çelikesir *et al*., 2020; Akkurt *et al*., 2019; Özkaraca *et al.*, 2020a,b,c).

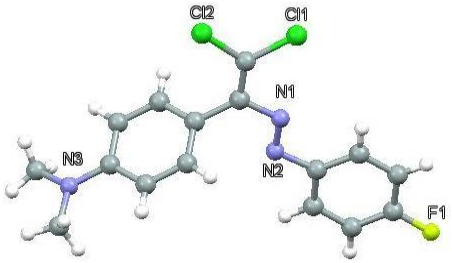
According to these benefits, we continued our research to synthesize dichlorodiazabutadienes which have dimethylamine group in aldehyde fragment and para-positioned halogen atoms in hydrazine fragment (Scheme 1). Also, we add that, dimethylamine group is an important chemical in making hair dyes. Our main purpose

in adding various para-positioned halogen atoms, is the importance of halogen-interactions in modern chemistry. Nowadays, this field is very important because of catalysis, medicinal engineering, nonlinear optics, reactivity and packing of functional supramolecular compounds. Making supramolecular materials is the main purpose of using non-covalent interactions. Adding halogen atom into main part in dichloroazadiene dyes completely changes crystal structure of dyes (Nenajdenko *et al*., 2020).

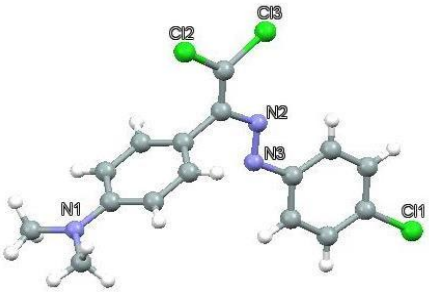


Scheme 1. General mechanism of synthesis of dichlorodiazabutadiens

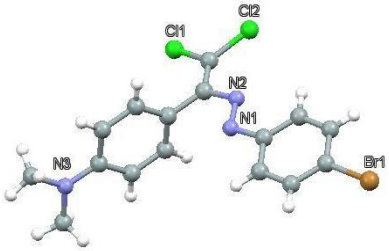
The spectras of the synthesized compounds **1-3** correspond to the literature datas [30]. Structures of synthesized compounds were confirmed by NMR and X-ray structural analysis (Figure 1-2).



4.(E)-4-(2,2-dichloro-1-((4fluorophenyl)diazenyl)vinyl)- N,N-dimethylaniline



5.(E)-4-(2,2-dichloro-1-((4chlorophenyl)diazinyl) vinyl)N,N-dimethylaniline.



6.(E)-4-(2,2-dichloro-1-((4-bromophenyl)diazenyl) vinyl)dimethylaniline

Figure 1. Molecular structures of 4-6.

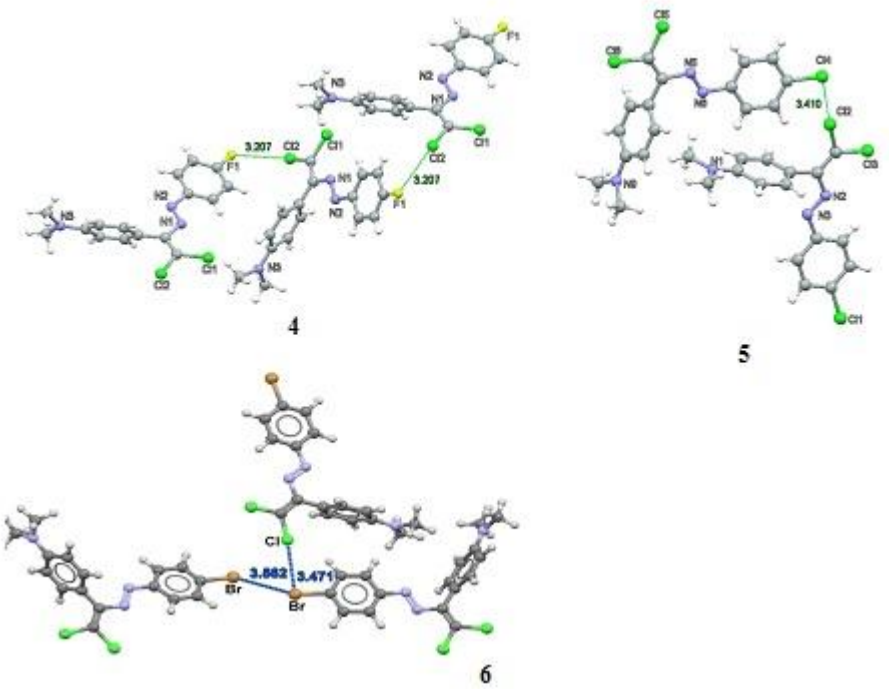


Figure 2. Describing intermolecular non-covalent interactions of 4-6.

As we can see, non-covalent interactions have an important role in crystal packing. Halogen atoms in hydrazine fragment create halogen interactions with dihalogen fragment to make crystal. In compound it's clear that, in 4 F-Cl bond [3.213 Å], in 5 CI···CI[3.410] and in 6 Br···Cl [3.471 Å]. Synthesis of (E)-4-{2,2-dichloro-1-[(p-halogenophenyl)diazenyl]vinyl}-N,N-dimethylanilines will be very important in dye industry because of non-covalent interactions and diaza group.

In a presence of catalytic olefinationphenylhydrazones which have been obtained from the reaction of 4-halogen substituted phenylhydrazines with p-N,N-dimetylbenzaldehyde form corresponding Eisomers of dichlorodiazadiene dyes. This shows selectivity of the reaction, which also explains importance of non-covalent halogen bondings in crystal packing. These bondings were confirmed not only by X-ray Structural Analysis, but also Hirshfeld surface analysis.

2. Experimental part

X-ray structural analysis of **4**,**5** and **6** compounds was carried out using of Bruker APEX II CCD diffractometer (T = 273 K, λMoKα-radiation, graphite monochromator, φ- and ω-scanned). The ^{1}H and ^{13}C NMR spectra were obtained by the Bruker Advance 300 (working frequency 300 and 75 MHz solvents $CDCl_3$ and $DMSOd_6$). $SiMe_4$ was used as ainternalstandard, and NTX was carried out on the Silufol on UB-254, for visualization of the spots was used the $KMnO_4$ solution and UB lamp. Column chromatography was carried out using silicagel (Merck 63-200).

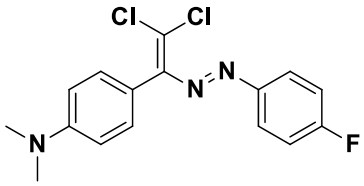
Synthesis of hydrazones

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 5 mmol of aldehyde

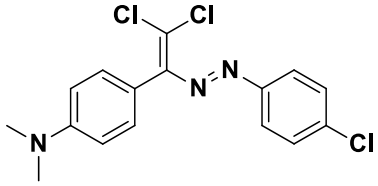
dropwise added and reaction mixture is stirred and heated. When the temperature reaches 78°C, the mixture is boiled for 5-10 minutes. Then, the reaction mixture is cooled to room temperature, 50 mL of distilled water is added to reaction mixture. Temperature reaches 60°C at intensive stirring. The reaction mixture wascooled to room temperature and filtered. If necessary, the residue of the product is washed with distilled water. The resulting hydrazine is dried at ambient temperature (15-20 hours).

General methods of synthesis of [(2,2-dichloro-1-phenylvinyl) diazenyl]phenyl)methanes

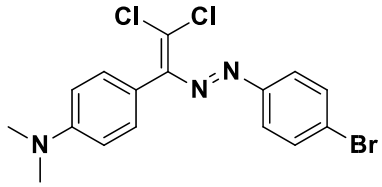
1 mmol of starting hydrazone is added to the flack, then 10-12 mL of DMSO, and then (290 mg; 1.25 mol/eq) TMEDA are added. Further catalyst CuCl (6 mg; 3 mol %) is added. Finally, CC_4 (4-5 mol / eq., 1.5 g) is added. The reaction mixture was stirred with magnetic stirrer. Typically, the reaction goes in 1.5 hours. The reaction mixture was poured into separatoryfunnel,then 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/n-hexane 1:5) is purificated by column chromatography method. Fractions containing the main reaction product identified by TLC.



Substance 4. (E)-4-{2,2-dichloro-1-[(4-fluorophenyl)diazenyl]vinyl}-N,N-dimethylaniline. red solid substance (yield 48 %), melting temp. 122123^0, Analytically calculated $C_{16}H_{14}Cl_2FN_3$(*M* = 338.20 ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.20 – 7.07 (m, 4H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.71, 131.08, 130.42, 128.97, 128.85, 125.34, 125.22, 124.68, 124.57, 119.46, 116.13, 115.83, 115.47, 115.17, 115.12, 111.49, 110.83, 43.94



Substance 5. (E)-4-{2,2-dichloro-1-[(4-chlorophenyl)diazenil]vinyl}-N,N-dimethylaniline. red solid substance (yield 52 %), melting temp. 135136^0, Analytically calculated $C_{16}H_{14}Cl_3N_3$ (*M* = 354.66),^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 3.05 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 152.41, 151.45, 150.29, 137.26, 135.11, 131.08, 129.27, 124.50, 119.11, 111.48, 40.29.



Substance 6. (E)-4-{1-[(4-bromophenyl)diazenyl]-2,2-dichlorovinyl}-N,N-dimethylaniline. red solid substance (yield 50 %), melting temp. 117118^0, Analytically calculated $C_{16}H_{14}BrCl_2N_3$(*M* = 399.11),^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.05 (s, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ 152.43, 151.80, 150.15, 135.28, 132.27, 131.12, 125.84, 124.72, 120.95, 111.66, 40.42.

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