

The structural properties of dichlorodiazadienes synthesized based on 4-methylbenzaldehyde

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Abstract

Dichlorodiazadienes were synthesized based on 4-methylbenzaldehyde, the structures of some compounds were confirmed via the X-ray method and a series of crystallographic properties, the role of non-covalent interactions in the forming of crystal, and (using Hirshfeld surface analysis) intermolecular interactions were studied. It was determined that as the result of the impact of nitro-group on the direction of the reactions of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)-hidrazone with CCl₄ and CBr₄, reaction by-products (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropan-2-yl)diazene, (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoyl chloride and (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoylbromide had been formed. While (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(3,4-dimethylphenyl)diazene crystallizes in the monoclinic *P*2₁/*n* space group with *Z* = 4, (E)-4-((2,2-dichloro-1-(p-tolyl)vinyl)diazenyl) benzonitrile crystallizes in the monoclinic *C**c* space group with four independent molecules (I, II, III and IV) in the asymmetric unit (*Z* = 16), and (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropan-2-yl)diazene and (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoylbromide crystallize in the monoclinic *P*2₁/*c* space group with *Z* = 4. The molecules in the crystal of (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(3,4-dimethylphenyl)diazene are linked into infinite three-dimensional network by C—H...N of hydrogen bonds, C---H... π and C---Cl... π interaction. In the crystal of the (E)-4-((2,2-dichloro-1-(p-tolyl)vinyl)diazenyl) benzonitrile, while molecules are linked in layers parallel to the (200) plane by intermolecular C---H...N hydrogen bonds and C---H... π interactions, in the crystal of the (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropan-2-yl)diazene, the molecules are connected in layers parallel to the (10-2) plane by intermolecular C---H...O hydrogen bonds, C---Cl... π and π - π interactions, and in the crystal of the (Z)-4-methyl-N-(4-

nitrophenyl)benzohydrazonylbromide, the molecules are connected in layers parallel to the (020) plane by intermolecular C---H...O and N---H...O hydrogen bonds and C--O... π interactions. These layers bond with van der Waals interactions, strengthening the crystal structure.

Keywords: 4-methylbenzaldehyde, Hirshfeld surface analysis, crystal structure, hydrogen bonds.

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1. Introduction

The synthesis and structural investigation of polyfunctional compounds is a highly focused and meticulously studied area within the field of fine organic synthesis. In this context, the synthesis of dihalogendiazabutadienes via the reaction of N-substituted hydrazones of benzaldehyde derivatives with polyhalomethanes (such as CCl₄ and CBr₄) in the presence of a CuCl catalyst has garnered significant attention. This process is particularly relevant due to its potential for structural exploration through X-ray crystallographic analysis and the study of factors influencing the reaction pathway (scheme 1).



Scheme 1. Synthesis of dihalogendiazabutadienes

Dihalogendiazabutadienes are notable for their high reactivity, which stems from their classification as heterodienes. The chemistry of heterodienes has long been a central topic in organic synthesis, with extensive literature exploring the behavior of related systems such as azoalkenes, nitrosoalkenes, α,β -unsaturated carbonyl compounds, and imines [6]. Heterodienes represent some of the simplest yet most valuable vinyl systems due to their distinctive reactivity, electronic structure, and synthetic utility [7]. The presence of heteroatoms within the conjugated diene framework induces polarization of the π -system, thereby enhancing their reactivity and enabling diverse reaction pathways [8].

A classification of the most commonly used heterodienes in organic synthesis—such as α,β -unsaturated carbonyl compounds (enones), 1- and 2-azadienes, 1,2-diaza-1,3-butadienes (azoalkenes), nitro- and nitrosoalkenes, 2,3-diaza-1,3-butadienes, α -dicarbonyl compounds, and α -diimines—has been previously established [8]. Notably, the azoalkene-type diene fragment synthesized by our research group is included in this classification.

In the literature, heterodienes are typically involved in two main types of reactions: (1) They act as highly reactive Michael acceptors in nucleophilic addition reactions [8,9], and (2) They undergo [4+2] cycloaddition (Diels–Alder) reactions with electron-rich dienophiles, owing to their electron-deficient nature [10–15].

Based on the above, it is evident that dihalogendiazabutadienes hold considerable promise as Michael acceptors in fine organic synthesis. The unique structures of the

halogendiazadienes synthesized by our group provide an excellent platform for investigating non-covalent interactions, which have become a significant area of contemporary research. The presence of geminal halogen atoms, a diazo group, and multiple electron-donating and electron-withdrawing substituents enables the formation of pnictogen [5], tetrel [2], and halogen bonding interactions [16,17], underscoring the importance of their synthesis.

Azo-hydrazone, in particular, are widely applied across various domains, ranging from catalysis [18], organic and inorganic synthesis [19,20], and medicinal chemistry [21] to materials science [22]. They also serve as molecular clocks [23], analytical reagents [24], ligands [25], and dyes [26]. The donor–acceptor properties of azo-hydrazone are largely governed by the nature of their functional groups [27–34]. Furthermore, upon halogenation, the formation of halogen bonds was observed, and the molecular and crystal structures, including intermolecular interactions, were thoroughly analyzed using Hirshfeld surface analysis.

2. Results and discussion

2.1. Synthesis of dichlorodiazadienes based on *p*-toluene benzaldehyde

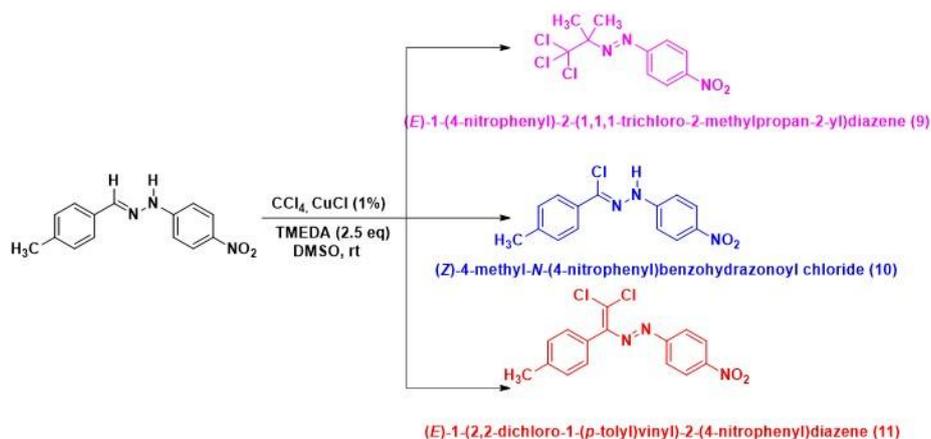
It is important to note that the impact of the nature of functional groups in N-substituted phenylhydrazones and their position in the benzene ring has always been in the focus of attention in our research. Precisely for this reason, all reaction products (whose presence in the reaction mixture was determined using TLC) were separated using column chromatography, and their structures were determined. Thus, the determination of obtaining by-products of the reaction allowed to get a more clear understanding of reaction mechanism, of the general course of the reaction [catalysis]. Precisely because of this research we determined the formation of several by-products in a series of reactions [35]. As a result of the research, it was concluded that the nature of functional groups in aldehyde fragment substantially affects the direction and yield of the reaction.

Various dichlorodiazadienes were synthesized via the reaction of N-substituted hydrazones [36] (synthesized from *p*-toluenebenzaldehyde) with CCl_4 under the conditions of catalytic olefination reaction, in the presence of CuCl in catalytic quantity.



Scheme 2. The synthesis of dichlorodiazadienes

The structure of obtained compounds 1-8 was confirmed using NMR. The monocrystals of compounds 4 and 6 were grown and their molecular structures were confirmed using X-ray structural analysis. However, it was determined that during the reaction of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)-hydrazone with an electronacceptor nitro-group in the hydrazone fragment, (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropan-2-yl)diazene and (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazoneyl chloride are formed together with the main reaction product, (E)-1-(2,2-dichloro-1-(*p*-tolyl)vinyl)-2-(4-nitrophenyl)diazene. The monocrystal of compound 9 was grown and its structure was confirmed using X-ray analysis method (scheme 3, figure 1).



Scheme 3. The scheme of the reaction of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine with CCl_4

It should be noted that in the course of the reaction of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine 9 with CBr_4 , the substitution of hydrogen atom of $=\text{CH}$ imine for bromine occurred.



Scheme 4. The synthesis of (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoyl bromide

The structure of (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoyl was confirmed using NMR, as well as X-ray analysis method. In both reactions of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)-hydrazone (meaning both with CCl_4 and with CBr_4), the proceeding of the reaction in the new direction, with the halogenation of the hydrogen atom on the imine carbon atom, was determined. Thus, taking into account all these results, it was proven that in the course of the reaction with (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)-hydrazone, 3 products are formed, which shows the substantial impact of nitro-group in the para-position in the hydrazine fragment on the direction of the reaction. It bears mentioning that these deviations have not been observed in other reactions

2.2 NMR interpretation

First, N-substituted phenylhydrazones were synthesized and their structures studied via NMR method. NMR spectres of hydrazones were in accordance with those reported in literature [36].

Then the corresponding dichlorodiazadienes were synthesized via reaction of phenylhydrazones with CCl_4 and their structures were also interpreted using NMR method. The fact that signals corresponding to NH and CH groups are non-existent in NMR ^1H spectre of dichlorodiazadienes shows the functionalization of $\text{C}(\text{sp}^2)\text{-H}$ bond in the compound. The existence of additional 1 C atom in the 150.81-162.32 range of ^{13}C specter shows the formation of this double bond.

The fact that a singlet corresponding to 6H atom characteristic of aliphatic CH_3 groups in the ^1H NMR specter of (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropane-2-yl)diazene (compound 9) can be observed at 1.67 m.h., and also the fact that there are 2

duplets at 8.39- 8.36 and 7.91 -7.88 m.h. shows that (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropane-2-yl)diazene compound is obtained.

The locations and splitting of signals (7.81 m.h. (1H,s), 2.41m.h. (3H s), 8.22-8.19 (2H d), 7.62-7.60 (2H d), 7.26-7.23 (2H d), 7.16-7.13 (2H d)) in the ¹H NMR specter demonstrates that the spectre belongs to (Z)-4-methyl-N(4-nitrophenyl)benzohydrazonyl chloride (compound 10).

2.3 Crystal structures

Structures of the synthesized compounds have been studied by a number of analytical methods, one of which was X-ray crystallographic method [37]. The molecular structures of compounds 4, 6, 9 and 12 are presented in Figure 1. Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Center (CCDC 2333633, 2367476, 2367477 and 2367479 for 4, for 6, or 9, for 12). Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336033. The crystallographic-structure data of the substances are presented in table 1.

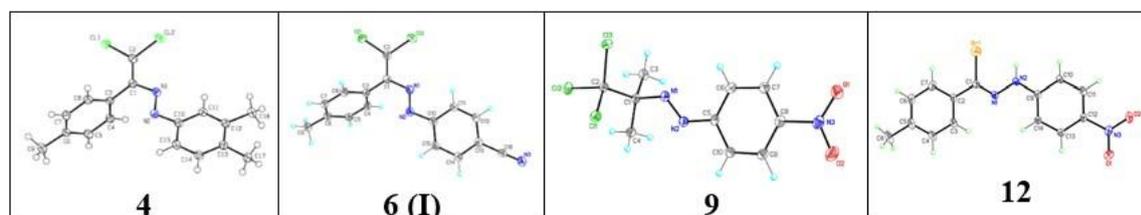


Figure 1. X-ray crystallographic structures of dichlorodiazadienes 4, 6 (I), 9 and 12

Crystal structure determination

While compound (4) crystallizes in the monoclinic $P2_1/n$ space group with $Z = 4$, compound (6) crystallizes in the monoclinic Cc space group with four independent molecules (I, II, III and IV) in the asymmetric unit ($Z = 16$), and compounds (9) and (12) crystallize in the monoclinic $P2_1/c$ space group with $Z = 4$.

In compound (4) (figure 1) the angle between the two aromatic rings (C3—C8 and C10—C15) in the molecule is $89.44(6)^\circ$. The C1--N1--N2--C10, C2--C1--N1--N2 and C3--C1--N1--N2 torsion angles are $178.31(10)$, $-170.01(11)$ and $12.48(16)^\circ$, respectively.

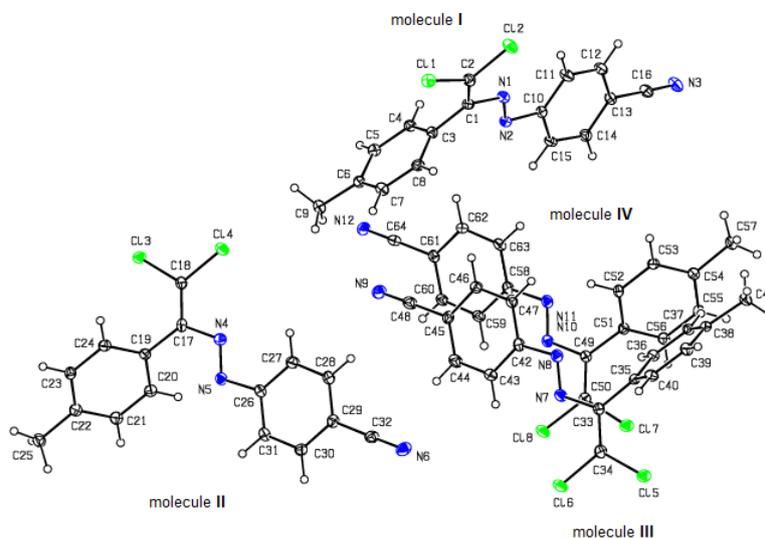


Figure 2. View of four molecules of compound (6) from the asymmetric unit with anisotropic displacement ellipsoids at the 30% probability level

The compound (6) (figure 1) has four independent molecules (I with N3, II with N6, III with N9 and IV with N12) in the asymmetric unit (figure 2). An overlay fit of inverted molecules II, III and IV on molecule I is shown in f 3, the weighted r.m.s. fit of the 21 non-H atoms being 0.903 Å and showing the major differences to be in the terminal phenyl groups (I: C10–C15, II: C26–C31, III: C42–C47 and IV: C58–C63) attached to the cyano groups of the molecules I, II, III and IV.

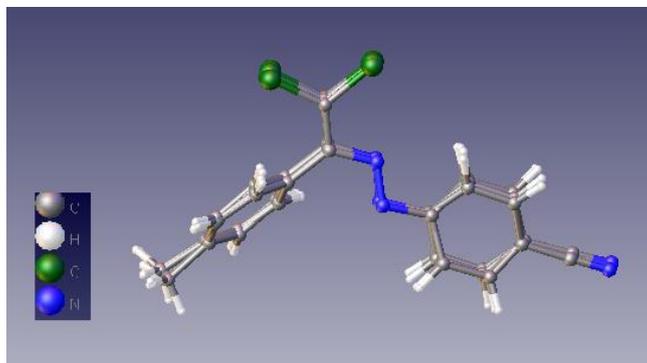


Figure 3. A least-squares overlay of the four independent molecules (6)

In the compound (6), the angles between the aromatic rings are $67.8(3)^\circ$ for (I), $55.7(2)^\circ$ for (II), $59.3(3)^\circ$ for (III) and $47.1(2)^\circ$ for (IV), respectively. The C1--N1--N2--C10, C2--C1--N1--N2 and C3--C1--N1--N2 torsion angles are $178.5(5)$, $-174.0(5)$ and $9.9(8)^\circ$, respectively for (I), C17--N4--N5--C26, C18--C17--N4--N5 and C19--C17--N4--N5 torsion angles are $-178.3(5)$, $-178.7(5)$ and $-0.9(8)^\circ$, respectively for (II), C33--N7--N8--C42, C34--C33--N7--N8 and C35--C33--N7--N8 torsion angles are $177.1(5)$, $-175.3(5)$ and $-9.1(8)^\circ$, respectively for (III) and C49--N10--N11--C58, C50--C49--N10--N11 and C51--C49--N10--N11 torsion angles are $179.0(5)$, $-179.4(5)$ and $1.1(8)^\circ$, respectively for (IV).

In compound (9) (figure 1), the C1--N1--N2--C5, C2--C1--N1--N2, C3--C1--N1--N2 and C4--C1--N1--N2 torsion angles are $177.53(11)$, $-133.24(12)$, $109.45(13)$ and $-12.37(16)^\circ$, respectively.

In compound (12) (figure 1), the angle between the two aromatic rings (C2—C7 and C9—C14) in the molecule is $10.03(17)^\circ$. The C1--N1--N2--C9, Br1--C1--N1--N2 and C2--C1--N1--N2 torsion angles are $-177.8(3)$, $-0.7(4)$ and $179.5(3)^\circ$, respectively. The molecular conformation is stabilized by intramolecular N---H...Br hydrogen contacts forming the S(5) ring motif.

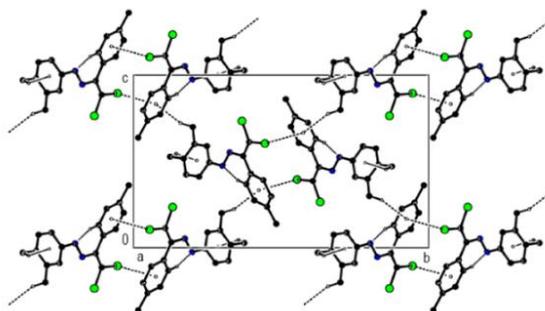


Figure 4. C---H... π and C--Cl... π interactions, and C---H...N bonds of compound (4) along the a-axis

The bond length and angle values for compound (4), (6), (9) and (12) are comparable with each other and with those of compounds reported in the literature [37-39].

In the crystal of compound (4), molecules are linked via intermolecular C---H...N hydrogen bonds, C---H... π and C---Cl... π [C2---Cl1...Cg1a : C2---Cl1 = $1.7145(12)$ Å,

C11...Cg1a = 3.4070(7), C2 ...Cg1a = 5.0174(12), C2---C11...Cg1a = 155.47(4)°; Symmetry code (a) - x, 1 - y, 1 - z; where Cg1 is a centroid of the C3—C8 benzene ring] interactions, forming a three-dimensional network and ensuring the stability of molecular packaging (table 1, figures 4 and 5).

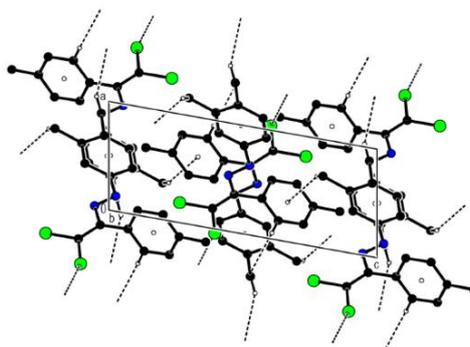


Figure 5. C---H... π and C---Cl... π interactions, and C---H...N bonds of compound (4) along the b-axis

Compound : 4				
D—H...A	D—H	H...A	D...A	D—H...A
C8—H8...N ⁱ	0.95	2.57	3.4894 (16)	163
C16---H16A...Cg1 ⁱⁱ	0.98	2.68	3.5406(15)	147
C17---H17A...Cg2 ⁱⁱⁱ	0.98	2.91	3.8286(16)	156
Symmetry code: (i) $-I+x, y, z$; (ii) $1/2+x, 3/2-y, -1/2+z$; (iii) $I+x, y, z$. Cg1 and Cg2 are the centroids of the C3—C8 and C5---C10 benzene rings, respectively.				
Compound : 6				
D—H...A	D—H	H...A	D...A	D—H...A
C12 H12 N9 ^{iv}	0.95	2.52	3.357(8)	147
C60 H60 N6 ^v	0.95	2.56	3.308(9)	136
C14 H14 Cg5 ^v	0.95	2.99	3.606(6)	124
C40 H40 Cg7 ^{vi}	0.95	2.98	3.700(4)	134
Symmetry codes: (iv) $x, 2-y, 1/2+z$; (v) $x, 1+y, z$; (vi) $x, -1+y, z$. Cg5 and Cg7 are the centroids of the centroids of the C35—C40 benzene ring for III and the C51---C56 benzene ring for IV, respectively.				
Compound : 9				
D—H...A	D—H	H...A	D...A	D—H...A
C3 H3A Cl3	0.98	2.69	3.1370(16)	108
C3 H3B O1 ^v	0.98	2.58	3.5208(18)	160
C4 H4B Cl2	0.98	2.68	3.1218(15)	107
C4 H4C Cl1	0.98	2.74	3.1571(15)	107
Symmetry code: (v) $x, 1+y, z$.				
Compound : 12				
D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...Br1	0.90	2.53	2.978 (3)	111
N2—H2...O1 ^{vii}	0.90	2.32	3.015 (4)	134
Symmetry code: (vii) $x+1, -y+1/2, z+1/2$.				

Table 1. Hydrogen-bond geometry (Å, °)

Compound (6) crystallizes in the monoclinic Cc space group with four symmetry-independent molecules in the asymmetric unit ($Z = 16$). The molecules are linked in layers parallel to the (200) plane by intermolecular C---H...N hydrogen bonds and C---H... π interactions (table 1, figures 6 and 7). These layers strengthen molecular packing by bonding with van der Waals interactions.

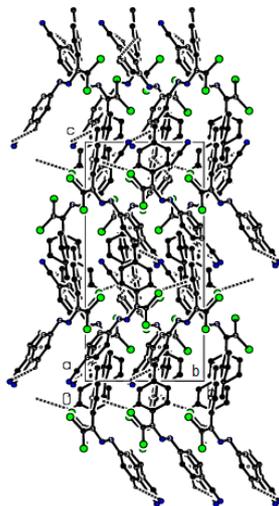


Figure 6. C---H... π and C---H...N interactions of compound (6) along the a-axis

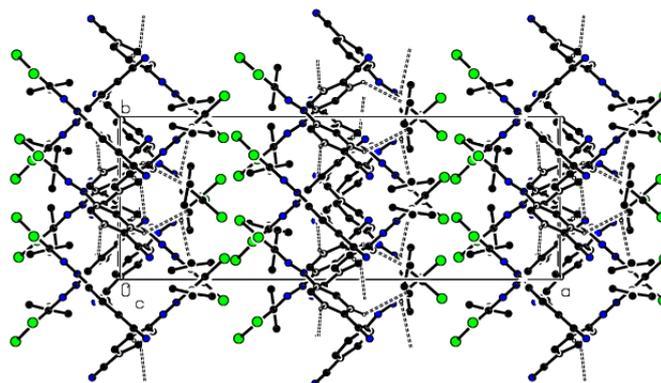


Figure 7. C---H... π and C---H...N interactions of compound (6) along the c-axis

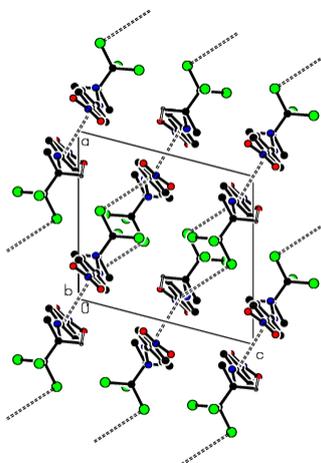


Figure 8. C---H...O, π - π and C---Cl... π interactions of compound (9) along the b-axis

Compound (9) crystallizes in the monoclinic $P2_1/c$ space group with $Z = 4$. The molecules are connected in layers parallel to the (10-2) plane by intermolecular C---H...O hydrogen bonds, C---Cl... π and π - π interactions ($Cg1...Cg1^a = 3.6269(8)$ Å; symmetry code (a) -x, 1-y, 1-z; where Cg1 is a centroid of the C5—C10 benzene ring) (table 1, figures 8 and 9). These layers bond with van der Waals interactions, strengthening the crystal structure.

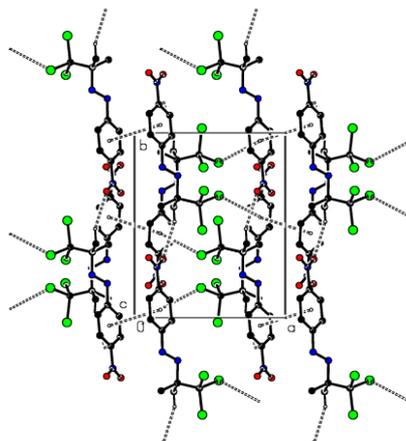


Figure 9. C---H...O, π - π and C---Cl... π interactions of compound (9) along the c-axis

Compound (12) crystallizes in the monoclinic $P2_1/c$ space group with $Z = 4$. The molecules are connected in layers parallel to the (020) plane by intermolecular C---H...O and N---H...O hydrogen bonds and C---O... π interactions (table 2, figures 10, 11 and 12). These layers bond with van der Waals interactions, strengthening the crystal structure.

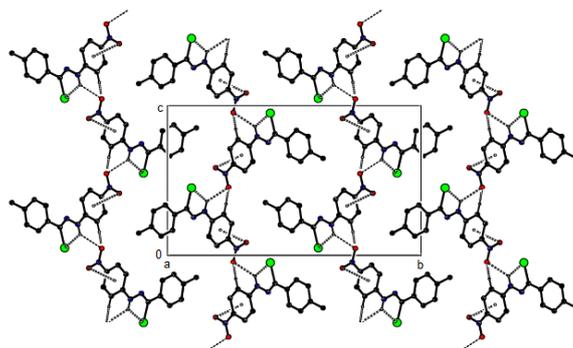


Figure 10. C---O... π , C---H...O and N---H...O interactions plus intra H-bonds of compound (12) along the a-axis

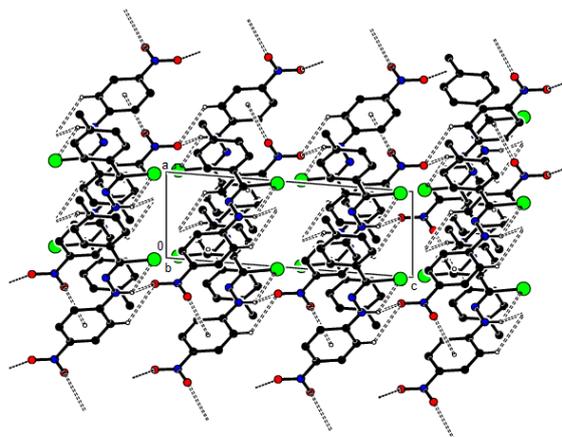


Figure 11. C---O... π , C---H...O and N---H...O interactions plus intra H-bonds along of compound (12) the b-axis

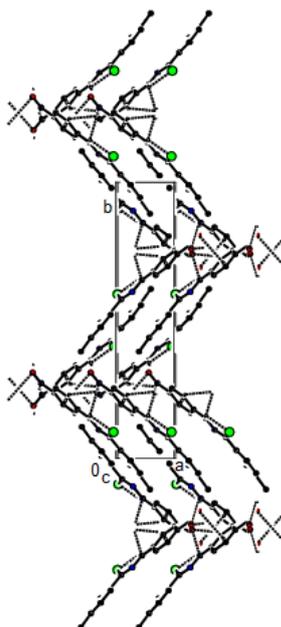


Figure 12. C---O... π , C---H...O and N---H...O interactions plus intra H-bonds along of compound (12) the c-axis

2.4. Hirshfeld surface analysis of (*e*)-1-(2,2-dichloro-1-(*p*-tolyl)vinyl)-2-(3,4-dimethylphenyl)diazene (compound 4).

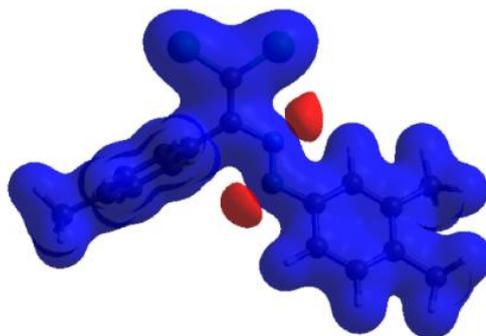


Figure 13. View of the three-dimensional Hirshfeld surface of the compound (4) plotted over d_{norm}

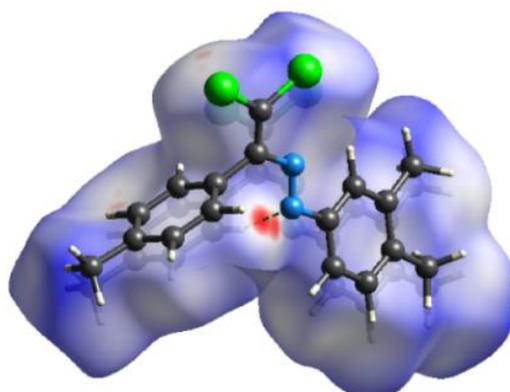


Figure 14. View of the three-dimensional Hirshfeld surface of the compound (4). plotted over electrostatic potential energy using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions around the atoms corresponding to positive and negative potentials, respectively

In order to visualize the intermolecular interactions in the crystal of the compound (4), a Hirshfeld surface analysis was carried out using *Crystal Explorer* (Version 17.5) [40]. In the Hirshfeld surface plotted over d_{norm} (figure 13), the white surface indicates contacts with distances equal to the sum of the van der Waals radii, and the red and blue colours indicate distances shorter or longer than the van der Waals radii, respectively [41]. The bright-red spots indicate their roles as the respective donors and/or acceptors; they also appear as blue and red regions corresponding to positive and negative potentials on the Hirshfeld surface mapped over electrostatic potential, as shown in figure 14. The blue regions indicate the positive electrostatic potential (hydrogen-bond donors), while the red regions indicate the negative electrostatic potential (hydrogen-bond acceptors).

The overall two-dimensional fingerprint plot, figure 15a, and those delineated into $\text{H}\cdots\text{H}$, $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ and $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ are illustrated in figures 15b–d, respectively, together with their relative contributions to the Hirshfeld surface. The most important interaction is $\text{H}\cdots\text{H}$, contributing 43.1% to the overall crystal packing, which is reflected in figure 15b as the widely scattered points of high density due to the large hydrogen content of the molecule with the tips at $d_e + d_i = 2.30 \text{ \AA}$.

The symmetrical pair of spikes resulting in the fingerprint plot delineated into $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ contacts [figure 15(c)] has a 23.0 % contribution to the HS with the tips at $d_e + d_i = 2.80 \text{ \AA}$. The $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ contacts, contributing 19.8 % to the overall crystal packing, are reflected in figure 15(d) with the tips at $d_e + d_i = 2.60 \text{ \AA}$. Finally, the $\text{H}\cdots\text{N}/\text{N}\cdots\text{H}$ (5.3 %), $\text{C}\cdots\text{Cl}/\text{Cl}\cdots\text{C}$ (3.6 %), $\text{C}\cdots\text{N}/\text{N}\cdots\text{C}$ (2.4%), $\text{Cl}\cdots\text{N}/\text{N}\cdots\text{Cl}$ (1.4%), $\text{C}\cdots\text{C}$ (0.7%) and $\text{Cl}\cdots\text{Cl}$ (0.6%) contacts to the Hirshfeld surface have very low distributions of points.

The large number of $\text{H}\cdots\text{H}$, $\text{H}\cdots\text{Cl}/\text{Cl}\cdots\text{H}$ and $\text{H}\cdots\text{C}/\text{C}\cdots\text{H}$ interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing [41].

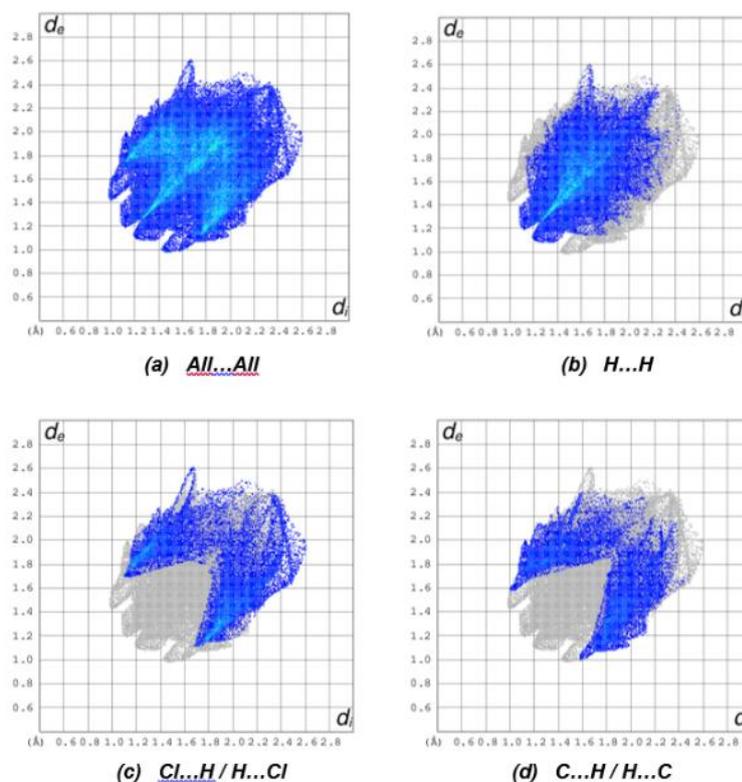


Figure 15. The full two-dimensional fingerprint plots for the compound (4), showing (a) all interactions, and delineated into (b) $\text{H}\cdots\text{H}$, (c) $\text{Cl}\cdots\text{H} / \text{H}\cdots\text{Cl}$ and (d) $\text{C}\cdots\text{H} / \text{H}\cdots\text{C}$ interactions. The d_i and d_e values are the closest internal and external distances (in \AA) from given points on the Hirshfeld surface contacts

Experimental part

2.5. General remarks

The syntheses of compounds were carried out at the Chemistry Department of Baku State University (Azerbaijan). Unless stated otherwise, all the reagents used in this study were obtained from the commercial sources (Aldrich, TCI-Europe, Strem, ABCR). The Hirshfeld surface analysis of compound (4) has been performed by using the Crystal Explorer program (version 17.5, Perth, Australia) [40]. The normalized contact distances (d_{norm}) based on Bondi's van der Waals radii [41] were mapped into the Hirshfeld surfaces. SiMe₄ (TMS) was used as an internal standard. Thin-layer chromatography (TLC) was performed on silhouette plate UB-254 and acidified KMnO₄ solution; UV lamp rays were used to make spots visible. Column chromatography was performed on silica gel of Merk firm (63-200). All compounds were crystallized from a methylene chloride and hexane (1:3, 1:5) solvent system.

2.6. NMR analysis

The NMR experiments have been performed on a BRUKER FT NMR spectrometer AVANCE 300 (Bruker, Karlsruhe, Germany) (300 MHz for ¹H and 75 MHz for ¹³C) with a BVT 3200 variable temperature unit in 5 mm sample tubes using Bruker standard software (TopSpin 3.1). Chemical shifts were given in ppm (δ) and were referenced to internal tetramethylsilane (TMS). Multiplicities are declared as follow: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet). Coupling constants J are given in Hz. The experimental parameters for ¹H are as follows: digital resolution = 0.23 Hz, SWH = 7530 Hz, TD = 32 K, SI = 16 K, 90° pulse-length = 10 ms, PL1 = 3 dB, ns = 1, ds = 0, d1 = 1 s and for ¹³C as follows: digital resolution = 0.27 Hz, SWH = 17 985 Hz, TD = 64 K, SI = 32 K, 90° pulse length = 9 ms, PL1 = 1.5 dB, ns = 100, ds = 2, d1 = 3 s. The NMR-grade DMSO-d₆ (99.7%, containing 0.3% H₂O), CDCl₃, CD₃OD was used for the solutions of synthesized compound

2.7. X-RAY analysis

The data collection for single-crystal structure analysis was performed using an XtaLAB Synergy, Dualflex, HyPix diffractometer from Rigaku with Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. The crystallographic data are summarized in table 2. Data were corrected for Lorentz, polarisation and absorption factors. The structure was solved by direct methods and refined using SHELXT and SHELXL [38,44]. All H atoms were geometrically fixed and allowed to ride on their parent C atoms with C---H = 0.95 - 0.98 \AA , and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ of the attached C atoms for methyl H atoms and 1.2 U_{eq} for aromatic H atoms.

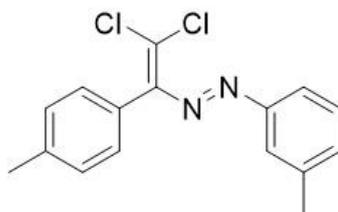
Compound	(4)	(6)	(9)	(12)
CCDC Deposition Number	2333633	2367476	2367477	2367479
Chemical formula	C ₁₇ H ₁₆ Cl ₂ N ₂	C ₁₆ H ₁₁ Cl ₂ N ₃	C ₁₀ H ₁₀ Cl ₃ N ₃ O ₂	C ₁₄ H ₁₂ BrN ₃ O ₂
M_r	319.22	316.18	310.56	334.17
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, Cc	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	100	100	100
a, b, c (\AA)	5.36140 (2), 22.28437 (9), 13.35931 (5)	30.631 (2), 9.7760 (3), 23.1022 (15)	10.18059 (17), 12.17071 (15), 10.84691 (18)	4.63166 (9), 22.1515 (5), 13.2146 (3)
β ($^\circ$)	100.1418 (4)	120.688 (9)	104.7276 (17)	94.5832 (19)
V (\AA^3)	1571.17 (1)	5949.1 (8)	1299.83 (4)	1351.46 (5)
Z	4	16	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	3.66	3.89	6.39	4.20

Crystal size (mm)	0.21 × 0.15 × 0.09	0.40 × 0.07 × 0.02	0.22 × 0.08 × 0.06	0.38 × 0.05 × 0.02
Diffractionmeter	XtaLAB Synergy, Dualflex, HyPix	Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector	Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector	Rigaku XtaLAB Synergy-S, HyPix-6000HE area-detector
Absorption correction	Multi-scan <i>CrysAlis PRO</i> 1.171.41.117a [45] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Gaussian <i>CrysAlis PRO</i> 1.171.43.117a [45] Numerical absorption correction based on gaussian integration over a multifaceted crystal model.	Gaussian <i>CrysAlis PRO</i> 1.171.43.92a (45) Numerical absorption correction based on gaussian integration over a multifaceted crystal model.	Gaussian <i>CrysAlis PRO</i> 1.171.43.92a (45) Numerical absorption correction based on gaussian integration over a multifaceted crystal model.
T_{\min}, T_{\max}	0.590, 1.000	0.317, 1.000	0.515, 1.000	0.387, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	71187, 3411, 3341	24351, 10616, 9291	14412, 2820, 2686	14624, 2864, 2694
R_{int}	0.038	0.050	0.034	0.049
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.638	0.638	0.638	0.639
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.077, 1.11	0.042, 0.107, 1.03	0.027, 0.077, 1.09	0.066, 0.177, 1.01
No. of reflections	3411	10616	2820	2864
No. of parameters	194	762	165	182
No. of restraints	0	2	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{\AA}^{-3}$)	0.29, -0.23	0.31, -0.36	0.38, -0.33	0.93, -0.75
Absolute structure	–	Refined as an inversion twin.	–	–
Absolute structure parameter	–	0.396 (16)	–	–

Table 2. Experimental details

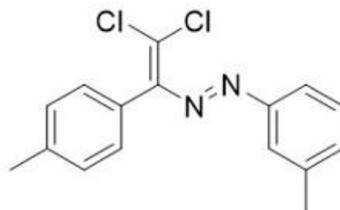
2.8. General procedure for synthesis of dichlorodiazadienes

Compounds were synthesized according to the reported method [1-5]. A 20-mL screw neck vial was charged with DMSO (10 mL), obtained hydrazones (1mmol) [36], respectively, tetramethylethylenediamine (TMEDA) (295 mg, 2.5mmol), CuCl (2 mg, 0.02 mmol) and CCl₄ (20 mmol, 10 equiv). After 1-3 hours (until TLC analysis showed complete consumption of the corresponding Schiff base), the reaction mixture was poured into an ~0.01 M solution of HCl (100 mL, ~pH 2- 3), and extracted with dichloromethane (3x20 mL). The combined organic phase was washed with water (3x50mL), followed by brine (30 mL), dried over anhydrous Na₂SO₄ and concentrated in vacuo by rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3/1-1/1), and the corresponding diazenes were obtained. Single crystal of the substances was prepared from a mixture of n-hexane and CH₂Cl₂ solvents by slow evaporation.



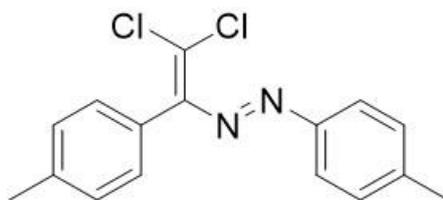
Compound 1. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-phenyldiazene

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-phenylhydrazine to afford the title compound an orange solid. Yield 51 %. M.p. 99°C. Anal. Calcd for C₁₅H₁₂Cl₂N₂ (M=290,17). ¹H NMR (300 MHz, Chloroform-d) δ 7.80 (d, *J* = 8.8 Hz, 2H, arom), 7.50 – 7.42 (m, 3H, arom), 7.26 (s, 2H, arom), 7.11 (d, *J* = 7.9 Hz, 2H, arom), 2.43 (s, 3H, CH₃), ¹³C NMR (75 MHz, CDCl₃) δ 162.3 (C_{Ar}), 152.9 (C), 152.2 (C), 138.6 (C_{Ar}), 135.2 (C_{Ar}), 131.5 (C_{Ar}), 129.8 (C_{Ar}H), 129.0 (C_{Ar}H), 128.9 (C_{Ar}H), 123.2 (C_{Ar}H), 21.5 (CH₃).



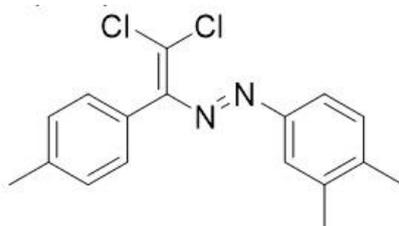
Compound 2. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(m-tolyl)diazene

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(m-tolyl)hydrazine to afford the title compound a red solid. Yield 69 %. M.p. 87°C. Anal. Calcd for C₁₆H₁₄Cl₂N₂ (M=305,20), ¹H NMR (300 MHz, Chloroform-d) δ 7.75 (s, 2H, arom), 7.44 (t, *J* = 7.9 Hz, 1H, arom), 7.36 (d, *J* = 7.7 Hz, 3H, arom), 7.22 (d, *J* = 8.0 Hz, 2H, arom), 2.51 (s, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 153.1 (C), 152.4 (C), 138.9 (C_{Ar}), 138.6 (C_{Ar}), 134.9 (C_{Ar}), 132.4 (C_{Ar}), 130.0 (C_{Ar}H), 129.7 (C_{Ar}), 129.0 (C_{Ar}H), 128.9 (C_{Ar}), 124.1 (C_{Ar}H), 120.3 (C_{Ar}H), 21.6 (CH₃), 21.4 (CH₃).



Compound 3. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(p-tolyl)diazene

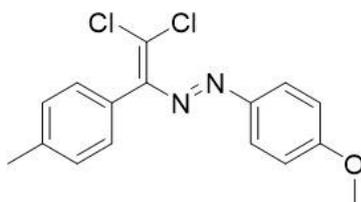
The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(p-tolyl)hydrazine to afford the title compound a red solid. Yield 75 %. M.p. 74°C. Anal. Calcd for C₁₆H₁₄Cl₂N₂ (M=305,20), ¹H NMR (300 MHz, Chloroform-d) δ 7.70 (d, *J* = 8.2 Hz, 2H, arom), 7.31 – 7.22 (m, 4H, arom), 7.10 (d, *J* = 7.9 Hz, 2H, arom), 2.42 (d, *J* = 3.1 Hz, 6H, (CH₃)). ¹³C NMR (75 MHz, CDCl₃) δ 151.1 (C), 142.2(C), 138.5 (C_{Ar}), 130.2 (C_{Ar}), 129.9 (C_{Ar}H), 129.6 (C_{Ar}H), 129.2(C_{Ar}), 128.8 (C_{Ar}H),, 128.2 (C_{Ar}), 123.2 (C_{Ar}H),, 21.4 (CH₃).



Compound 4. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(3,4-dimethylphenyl)diazene

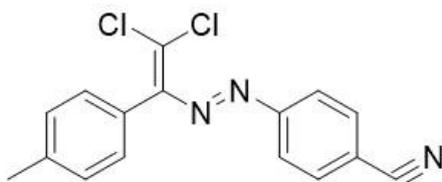
The title compound was prepared according to the general procedure using (E)-1-(3,4-dimethylphenyl)-2-(4-methylbenzylidene)hydrazine to afford the title compound a orange solid. Yield 51 %. M.p. 73°C. Anal. Calcd for C₁₇H₁₆Cl₂N₂ (M=319,22). ¹H NMR (300 MHz, Chloroform-d, ppm) δ 7.55 (d, *J* = 14.2 Hz, 2H, arom), 7.26 – 7.15 (m, 3H, arom), 7.09

(d, $J = 7.7$ Hz, 2H, arom), 2.42 (s, 3H, CH₃), 2.31 (s, 6H, 3,4-(CH₃)₂). ¹³C NMR (75 MHz, CDCl₃, ppm) δ 162.3 (C), 162.1 (C), 140.9 (C_{Ar}), 137.3 (C_{Ar}), 134.5 (C_{Ar}), 130.1 (C_{Ar}H), 129.8 (C_{Ar}H), 129.6 (C_{Ar}), 128.8 (C_{Ar}H), 124.5 (C_{Ar}H), 121.3 (C_{Ar}), 120.6 (C_{Ar}H), 21.4 (CH₃), 19.9 (3,4-(CH₃)₂), 19.7(3,4-(CH₃)₂). CCDC reference 2268431.



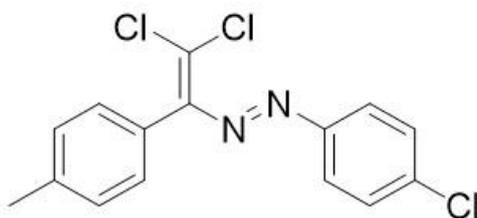
Compound 5. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(4-methoxyphenyl)diazene

The title compound was prepared according to the general procedure using (E)-1-(4-methoxyphenyl)-2-(4-methylbenzylidene)hydrazine to afford the title compound a red solid. Yield 63 %. M.p. 104°C. Anal. Calcd for C₁₆H₁₄Cl₂N₂O (M=321,20). ¹H NMR (300 MHz, Chloroform-d, ppm) δ 7.79 (d, $J = 9.0$ Hz, 2H, arom), 7.26 (d, $J = 8.0$ Hz, 2H, arom), 7.10 (d, $J = 8.0$ Hz, 2H, arom), 6.95 (d, $J = 9.0$ Hz, 2H, arom), 3.88 (s, 3H, OCH₃), 2.42 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃, ppm) δ 155.9 (C), 155.0 (C), 147.4 (C_{Ar}), 138.4 (C_{Ar}), 138.1 (C_{Ar}), 129.9 (C_{Ar}H), 129.7 (C_{Ar}), 128.8 (C_{Ar}H), 125.2 (C_{Ar}H), 114.1 (C_{Ar}H), 55.5 (OCH₃), 21.4 (CH₃). CCDC reference 1984582.



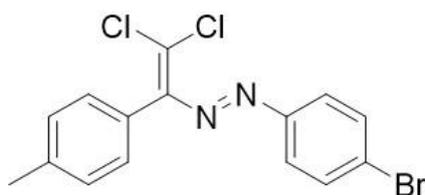
Compound 6. (E)-4-((2,2-dichloro-1-(p-tolyl)vinyl)diazenyl) benzonitrile

The title compound was prepared according to the general procedure using (E)-4-(2-(4-methylbenzylidene)hydrazineyl)benzonitrile to afford the title compound a red solid. Yield 69 %. M.p. 87°C. Anal. Calcd for C₁₆H₁₁Cl₂N₃ (M= 316,19). ¹H NMR (300 MHz, Chloroform-d) δ 7.86 (d, $J = 8.5$ Hz, 2H, arom), 7.75 (d, $J = 8.5$ Hz, 2H, arom), 7.27 (d, $J = 6.6$ Hz, 2H, arom), 7.08 (d, $J = 8.0$ Hz, 2H, arom), 2.43 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 162.3 (C_{Ar}), 158.2 (C_{Ar}), 154.7 (C_{Ar}), 139.0 (C_{Ar}), 133.1 (C_{Ar}H), 129.7 (C_{Ar}H), 129.0 (C_{Ar}H), 128.7(C_{Ar}), 123.6 (C_{Ar}H), 118.4 (C_{Ar}), 114.2 (C_{Ar}), 21.5 (-CH₃).



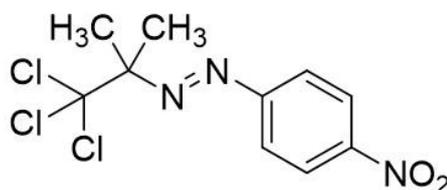
Compound 7. (E)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-(p-tolyl)vinyl)diazene

The title compound was prepared according to the general procedure using (E)-1-(4-chlorophenyl)-2-(4-methylbenzylidene)hydrazine to afford the title compound a red solid. Yield 69 %. M.p. 87°C. Anal. Calcd for C₁₅H₁₁Cl₃N₂ (M= 325,62), ¹H NMR (300 MHz, Chloroform-d, ppm) δ 7.76 (d, $J = 8.5$ Hz, 2H, arom), 7.44 (d, $J = 8.5$ Hz, 2H, arom), 7.28 (d, $J = 7.7$ Hz, 2H, arom), 7.11 (d, $J = 7.8$ Hz, 2H, arom), 2.45 (s, 3H, -CH₃). ¹³C NMR (75 MHz, CDCl₃, ppm) δ 152.3(C), 151.3(C), 138.7 (C_{Ar}), 137.4 (C_{Ar}), 129.8 (C_{Ar}H), 129.3 (C_{Ar}H), 129.0 (C_{Ar}H), 128.6 (C_{Ar}), 128.3 (C_{Ar}), 124.4 (C_{Ar}H), 123.8 (C_{Ar}), 21.5 (-CH₃).



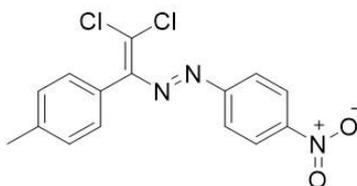
Compound 8. (E)-1-(4-bromophenyl)-2-(2,2-dichloro-1-(p-tolyl)vinyl)diazene

The title compound was prepared according to the general procedure using (E)-1-(4-bromophenyl)-2-(4-methylbenzylidene)hydrazine to afford the title compound a red solid. Yield 56 %. M.p. 112°C. Anal. Calcd for $C_{16}H_{14}Cl_2N_2$ (M=305,20), 1H NMR (300 MHz, Chloroform-d) δ 7.72 – 7.55 (m, 1H, arom), 7.46 (d, J = 8.0 Hz, 3H, arom), 7.20 (d, J = 8.0 Hz, 4H, arom), 2.38 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.2 ($C_{Ar}H$), 129.8 ($C_{Ar}H$), 129.1 ($C_{Ar}H$), 128.9 (C_{Ar}), 128.5 (C_{Ar}), 128.0 (C_{Ar}), 126.8 (C), 126.4 (C), 125.4 (C_{Ar}), 124.6 ($C_{Ar}H$), 29.7(CH_3).



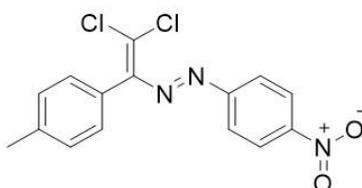
Compound 9. (E)-1-(4-nitrophenyl)-2-(1,1,1-trichloro-2-methylpropan-2-yl)diazene

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine to afford the title compound a red solid. Yield 22 %. M.p.63°C. Anal. Calcd for $C_{10}H_{10}Cl_3N_3O_2$ (M=310,55). 1H NMR (300 MHz, Chloroform-d) δ 8.38 (d, J = 9.0 Hz, 2H, arom), 7.89 (d, J = 9.0 Hz, 2H, arom), 1.67 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (C_{Ar}), 134.0(C_{Ar}), 124.7 ($C_{Ar}H$), 123.3 ($C_{Ar}H$), 82.8 ($C(CH_3)_2$), 52.2 (CCl_3), 22.2(CH_3)₂.



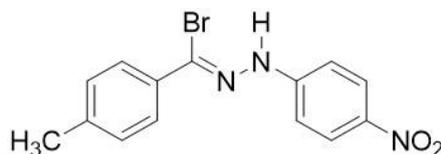
Compound 10. (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoyl chloride

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine to afford the title compound a red solid. Yield 25 %. M.p. 182°C. Anal. Calcd for $C_{14}H_{12}ClN_3O_2$ (M=336,17). 1H NMR (300 MHz, Chloroform-d) δ 8.21 (d, J = 9.2 Hz, 2H, arom), 7.81 (s, 1H, -NH), 7.61 (d, J = 8.1 Hz, 2H, arom), 7.24 (d, J = 7.9 Hz, 2H, arom), 7.14 (d, J = 9.1 Hz, 2H, arom), 2.41 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (CCl), 150.3(C_{Ar}), 139.8(C_{Ar}), 131.9(C_{Ar}), 129.5($C_{Ar}H$), 126.7($C_{Ar}H$), 126.2($C_{Ar}H$), 111.6 ($C_{Ar}H$), 110.4, (C_{Ar}), 21.5. (- CH_3).



Compound 11. (E)-1-(2,2-dichloro-1-(p-tolyl)vinyl)-2-(4-nitrophenyl) diazene

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine to afford the title compound a red solid. Yield 45 %. M.p. 67°C. Anal. Calcd for C₁₅H₁₁Cl₂N₃O₂ (M=336,17). ¹H NMR (300 MHz, Chloroform-d) δ 8.32 (d, *J* = 9.0 Hz, 2H, arom), 7.90 (d, *J* = 9.0 Hz, 2H, arom), 7.28 (d, *J* = 7.7 Hz, 2H, arom), 7.08 (d, *J* = 7.9 Hz, 2H, arom), 2.44 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 165.9 (C_{Ar}), 162.3 (C_{Ar}), 151.8 (C_{Ar}), 149.1 (C_{Ar}), 144.0 (C_{Ar}), 129.7 (C_{Ar}H), 129.1 (C_{Ar}H), 127.8 (C_{Ar}), 124.6 (C_{Ar}H), 123.7 (C_{Ar}H), 116.3 (C_{Ar}), 29.7 (-CH₃).



Compound 12. (Z)-4-methyl-N-(4-nitrophenyl)benzohydrazonoylbromide

The title compound was prepared according to the general procedure using (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine to afford the title compound a red solid. Yield 56 %. M.p. 176°C. Anal. Calcd for C₁₄H₁₂ClN₃O₂ (M=336,17). ¹H NMR (300 MHz, Chloroform-d) δ 8.41 (s, 1H, -NH), 8.23 (d, *J* = 7.4 Hz, 2H, arom), 7.92 – 7.73 (m, 2H, arom), 7.27 – 7.21 (m, 3H, arom), 2.43 (s, 3H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 129.7 (C_{Ar}), 129.3 (C_{Ar}H), 128.0 (C_{Ar}H), 126.8 (C_{Ar}H), 126.1 (C_{Ar}H), 124.6 (C), 123.4 (C) 114.5 (C_{Ar}), 112.8 (C_{Ar}), 112.6 (C_{Ar}), 21.3 (-CH₃).

3. Conclusion

The new dichlorodiazadienes were synthesized and we were first to determine that reaction proceeds along the new direction, with the halogenation of the hydrogen atom on the imine carbon atom in both reactions of (E)-1-(4-methylbenzylidene)-2-(4-nitrophenyl)hydrazine with CCl₄ and CBr₄. In the crystal of compound (4), while molecules are linked into infinite three-dimensional network by C–H...N of hydrogen bonds, C---H...π and C---Cl...π interaction. In the crystal of the compound (6), molecules are linked in layers parallel to the (200) plane by intermolecular C---H...N hydrogen bonds and C---H...π interactions, in the crystal of the compound (9), the molecules are connected in layers parallel to the (10-2) plane by intermolecular C---H...O hydrogen bonds, C---Cl... π and π-π interactions, and in the crystal of the compound (12), the molecules are connected in layers parallel to the (020) plane by intermolecular C---H...O and N---H...O hydrogen bonds and C--O... π interactions. These layers bond with van der Waals interactions, strengthening the crystal structure. In addition, Hirshfeld surface analysis of compound (4) also revealed that the dominant interaction in the crystal structure is van der Waals interactions.

Author contributions

Conceptualization, N.Sh., A.Q., G.A. and A.M.; methodology, A.Q., G.A., S.M.; G.B., A.N. software, M.A.; validation, V.K and M.A , A.T.; writing—original draft preparation, N.Sh, G.A., M.A., V.N writing—review and editing, N.Sh., G.A, A.M. All authors have read and agreed to the published version of the manuscript

Authors' Declaration

The authors declare no conflict of interests regarding the publication of this article.

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