

# Crystal structure and Hirshfeld surface analysis of 4-{2,2-dichloro-1-[(*E*)-(4-fluorophenyl)diazenyl]-ethenyl}-*N,N*-dimethylaniline

Kadriye Özkaraca,<sup>a</sup> Mehmet Akkurt,<sup>b</sup> Namiq Q. Shikhaliyev,<sup>c</sup> Ulviyya F. Askerova,<sup>c</sup> Gulnar T. Suleymanova,<sup>c</sup> Irada M. Shikhaliyeva<sup>c</sup> and Ajaya Bhattarai<sup>d\*</sup>

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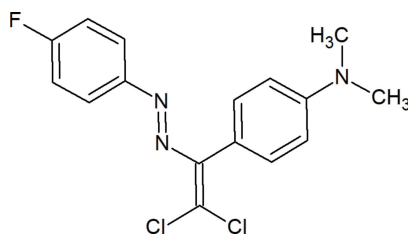
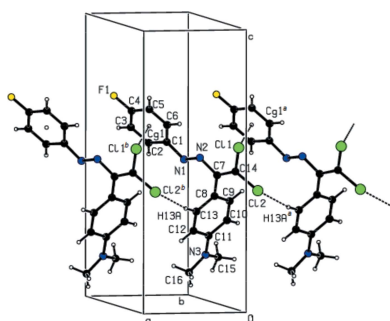
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<sup>a</sup>Institute of Natural and Applied Science, Erciyes University, 38039 Kayseri, Turkey, <sup>b</sup>Department of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, <sup>c</sup>Organic Chemistry Department, Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan, and <sup>d</sup>Department of Chemistry, M.M.A.M.C (Tribhuvan University), Biratnagar, Nepal. \*Correspondence e-mail: bkajaya@yahoo.com

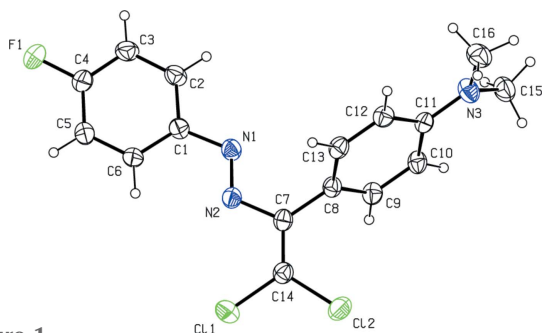
In the title compound, C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>FN<sub>3</sub>, the dihedral angle between the two aromatic rings is 64.12 (14)°. The crystal structure is stabilized by a short Cl···H contact, C—Cl··· $\pi$  and van der Waals interactions. The Hirshfeld surface analysis and two-dimensional fingerprint plots show that H···H (33.3%), Cl···H/H···Cl (22.9%) and C···H/H···C (15.5%) interactions are the most important contributors towards the crystal packing.

## 1. Chemical context

Both inter- and intramolecular weak interactions play a crucial role in determining the properties of organic compounds and controlling their molecular organization in solution and in the solid state, which is sensitive to their chemical environment, solvent polarity, temperature, *etc.* (Asadov *et al.*, 2016; Maharramov *et al.*, 2009, 2010; Mahmudov *et al.*, 2013, 2014*a,b*, 2015, 2017*a,b*, 2019; Shikhaliyev *et al.*, 2013, 2014). For example, in catalysis monomeric, oligomeric or polymeric compounds can promote various organic transformations not only by coordination bonds but also through non-covalent interactions, such as hydrogen, halogen, chalcogen, pnictogen, tetrel and triel bonds, as well as metal–metal, cation– $\pi$ , anion– $\pi$ , lone pair– $\pi$ ,  $\pi$ – $\pi$  stacking, agostic, pseudo-agostic, anagostic, dispersion-driven, lipophilic, *etc.* or their cooperation (Akbari Afkhami *et al.*, 2017; Gurbanov *et al.*, 2017, 2018; Kopylovich *et al.*, 2011*a,b*; Ma *et al.*, 2017*a,b*; Mahmoudi *et al.*, 2016, 2017*a,b,c*, 2018*a,b*). On the other hand, we and other researchers have attached various types of non-covalent-bond donor synthons to dye molecules, which results in interesting analytical and solvatochromic properties (Maharramov *et al.*, 2018; Mahmudov *et al.*, 2010, 2011; Mahmudov & Pombeiro, 2016).



In order to continue our work in this direction, we have functionalized a new azo dye, 4-{2,2-dichloro-1-[(*E*)-(4-



**Figure 1**  
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 30% probability level.

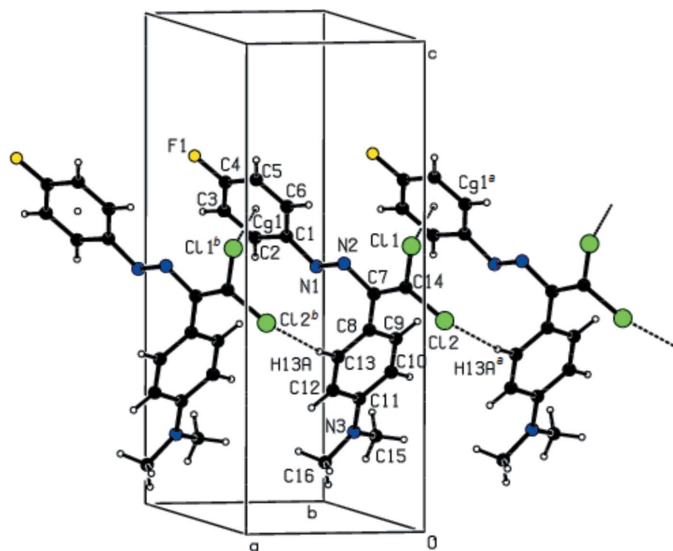
fluorophenyl)diazanyl]ethenyl]-*N,N*-dimethylaniline, which provides C–H···F and C–Cl···F types of intermolecular weak interactions.

## 2. Structural commentary

In the title compound (Fig. 1), the dihedral angle between the benzene rings (C1–C6 and C8–C13) of the 4-fluorophenyl and *N,N*-dimethylaniline groups is 64.12 (14)°. The amine N atom as well as the directly adjacent arene C atom are bent a little out of the plane of the other five aromatic C atoms, with deviations of 0.007 (3) Å for C11 and 0.027 (2) Å for N3. The N1–N2–C7–C14, N2–C7–C14–C11, N2–C7–C14–Cl2 and C8–C7–C14–Cl2 torsion angles are –172.0 (2), 2.1 (3), –177.0 (2) and 0.6 (4)°, respectively.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, the molecules are connected by a short Cl2···H13A contact (2.96 Å) and C–Cl··· $\pi$  interactions,



**Figure 2**  
A partial packing diagram of the title compound showing chain formation along the *a*-axis direction. Symmetry operators: (a)  $-1 + x, y, z$ ; (b)  $1 + x, y, z$ . Cg1 is the centroid of the C1–C6 ring.

**Table 1**  
C–Cl··· $\pi$  interaction geometry (Å, °).

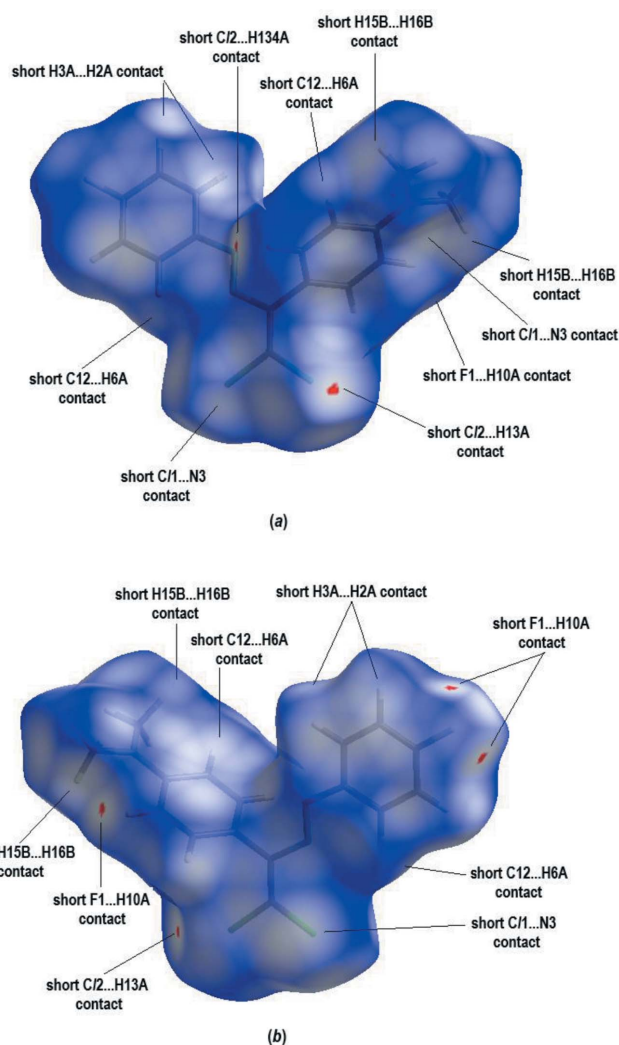
Cg1 is the centroid of the C1–C6 ring.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C14–Cl1···Cg1 <sup>i</sup>	1.72 (1)	3.93 (1)	3.882 (3)	76 (1)

Symmetry code: (i)  $x - 1, y, z$ .

which contribute to the overall packing energy stabilization, into infinite columns along the *a*-axis direction (Table 1; Fig. 2).

In order to visualize the intermolecular interactions in the crystal of the title compound, a Hirshfeld surface analysis (Hirshfeld, 1977; Spackman & Jayatilaka, 2009) was carried out using *CrystalExplorer17.5* (Turner *et al.*, 2017). Three-dimensional molecular Hirshfeld surfaces were generated using a ‘high standard’ surface resolution colour-mapped over the normalized contact distance. The red, white and blue regions visible on the  $d_{\text{norm}}$  surfaces indicate contacts with distances shorter, longer and equal to the van der Waals radii (Fig. 3).



**Figure 3**  
Front and back sides of the three-dimensional Hirshfeld surface of the title compound plotted over  $d_{\text{norm}}$  in the range 0.0350 to 0.8404 a.u.

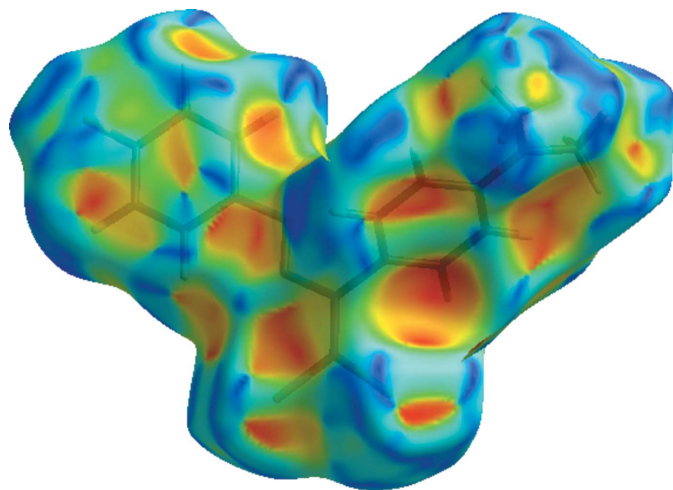
**Table 2**

Summary of short interatomic contacts (Å) in the title compound.

$A \cdots B$	Distance	Symmetry operation for $B$
H15B $\cdots$ H16B	2.45	$-1 + x, y, z$
Cl1 $\cdots$ N3	3.409 (3)	$-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
Cl2 $\cdots$ H6A	2.97	$\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
Cl2 $\cdots$ H13A	2.96	$-1 + x, y, z$
F1 $\cdots$ H10A	2.66	$\frac{3}{2} + x, \frac{3}{2} - y, 1 - z$
H3A $\cdots$ H2A	2.53	$\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$

The bright-red spots near atoms Cl2 and Cl3 in Fig. 3a refer to the short Cl2 $\cdots$ H13A contact, and near the atoms F1 and Cl10 in Fig. 3b to the F1 $\cdots$ H10A contact. The shape-index of the Hirshfeld surface is a tool to visualize the  $\pi$ - $\pi$  stacking by the presence of adjacent red and blue triangles; if there are no adjacent red and/or blue triangles, then there are no  $\pi$ - $\pi$  interactions. Fig. 4 clearly suggests that there are no  $\pi$ - $\pi$  interactions in the crystal structure.

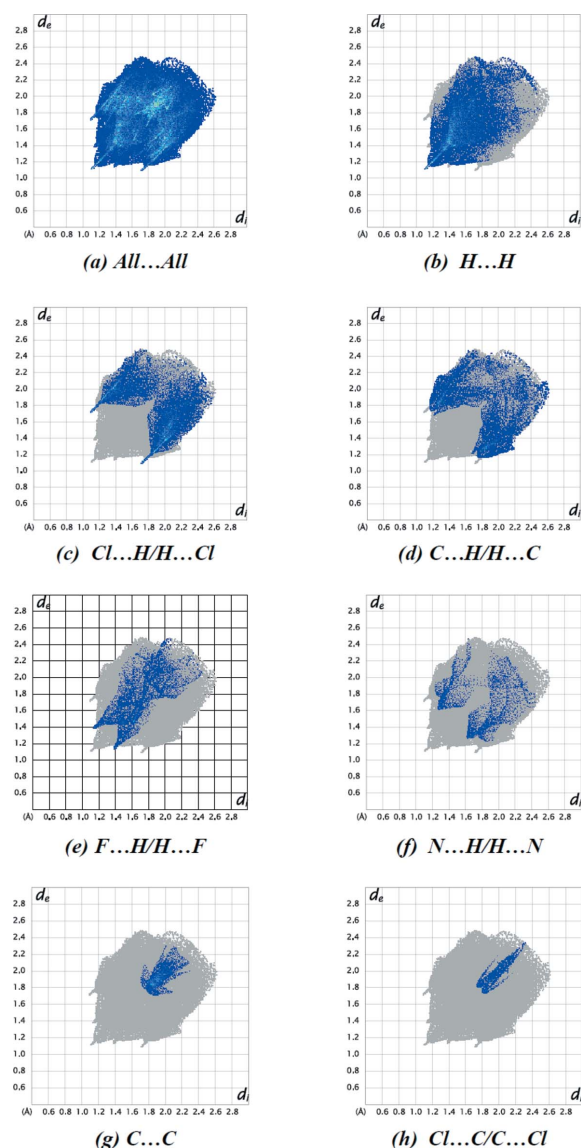
The overall two-dimensional fingerprint plot, Fig. 5a, and those delineated into H $\cdots$ H, Cl $\cdots$ H/H $\cdots$ Cl, C $\cdots$ H/H $\cdots$ C, F $\cdots$ H/H $\cdots$ F, N $\cdots$ H/H $\cdots$ N, C $\cdots$ C and Cl $\cdots$ C/C $\cdots$ Cl contacts (McKinnon *et al.*, 2007) are illustrated in Fig. 5b–h, together with their relative contributions to the Hirshfeld surface while details of the various contacts are given in Table 2. The most important interaction is H $\cdots$ H, contributing 33.3% to the overall crystal packing, which is reflected in Fig. 5b as widely scattered points of high density due to the large hydrogen content of the molecule with the tip at  $d_e = d_i = 1.10$  Å. The reciprocal Cl $\cdots$ H/H $\cdots$ Cl interactions appear as two symmetrical broad wings with  $d_e + d_i \simeq 2.80$  Å and contribute 22.9% to the Hirshfeld surface (Fig. 5c). The pair of characteristic wings in the fingerprint plot delineated into H $\cdots$ C/C $\cdots$ H contacts (Fig. 5d; 15.5% contribution to the Hirshfeld surface), have the tips at  $d_e + d_i \simeq 2.95$  Å. The fingerprint plot for F $\cdots$ H/H $\cdots$ F contacts (9.0% contribution), Fig. 5e, has a pair of spikes with the tips at  $d_e + d_i = 2.55$  Å. The remaining contributions from the other different interatomic contacts to the Hirshfeld surfaces are listed in Table 3. The small contri-


**Figure 4**  
 Hirshfeld surface of the title compound plotted over shape-index.

**Table 3**

Percentage contributions of interatomic contacts to the Hirshfeld surface for the title compound.

Contact	Percentage contribution
H $\cdots$ H	33.3
Cl $\cdots$ H/H $\cdots$ Cl	22.9
C $\cdots$ H/H $\cdots$ C	15.5
F $\cdots$ H/H $\cdots$ F	9.0
N $\cdots$ H/H $\cdots$ N	4.9
C $\cdots$ C	4.7
Cl $\cdots$ C/C $\cdots$ Cl	2.7
N $\cdots$ C/C $\cdots$ N	2.0
Cl $\cdots$ N/N $\cdots$ Cl	2.0
Cl $\cdots$ F/F $\cdots$ Cl	1.9
C $\cdots$ F/F $\cdots$ C	0.8
F $\cdots$ N/N $\cdots$ F	0.3


**Figure 5**

The full two-dimensional fingerprint plots for the title compound, showing (a) all interactions, and delineated into (b) H $\cdots$ H, (c) Cl $\cdots$ H/H $\cdots$ Cl, (d) C $\cdots$ H/H $\cdots$ C, (e) F $\cdots$ H/H $\cdots$ F, (f) N $\cdots$ H/H $\cdots$ N, (g) C $\cdots$ C and (h) Cl $\cdots$ C/C $\cdots$ Cl interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface.

bution of the other weak intermolecular N···H/H···N, C···C, Cl···C/C···Cl, N···C/C···N, Cl···N/N···Cl, Cl···F/F···Cl, C···F/F···C and F···N/N···F contacts has a negligible effect on the packing.

The Hirshfeld surface analysis confirms the importance of H-atom contacts in establishing the packing. The large number of H···H, Cl···H/H···Cl and C···H/H···C interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar *et al.*, 2015).

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.41, update of November 2019; Groom *et al.*, 2016) for structures having an (*E*)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene unit gave 25 hits. Six compounds closely resemble the title compound, *viz.* 1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (CSD refcode HONBOE; Akkurt *et al.*, 2019), 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (HONBUK; Akkurt *et al.*, 2019), 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-fluorophenyl)ethenyl]diazene (HODQAV; Shikhaliyev *et al.*, 2019), 1-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]-2-(4-fluorophenyl)diazene (XIZREG; Atioğlu *et al.*, 2019), 1,1-[methylenebis(4,1-phenylene)]bis[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (LEQXIR; Shikhaliyev *et al.*, 2018), 1,1-[methylenebis(4,1-phenylene)]bis[2,2-dichloro-1-(4-chlorophenyl)ethenyl]diazene (LEQXOX; Shikhaliyev *et al.*, 2018).

In the crystal structures of HONBOE and HONBUK, the aromatic rings form dihedral angles of 60.9 (2) and 64.1 (2)°, respectively. Molecules are linked through weak X···Cl contacts (X = Br for HONBOE and Cl for HONBUK) and C—H···Cl and C—Cl···π interactions into sheets parallel to the *ab* plane. Additional van der Waals interactions consolidate the three-dimensional packing. In the crystal of HODQAV, molecules are stacked in columns along the *a* axis via weak C—H···Cl hydrogen bonds and face-to-face π–π stacking interactions. The crystal packing is further stabilized by short Cl···Cl contacts. In XIZREG, molecules are linked by C—H···O hydrogen bonds into zigzag chains running along the *c*-axis direction. The crystal packing is further stabilized by C—Cl···π, C—F···π and N—O···π interactions. In the crystal of LEQXIR, C—H···N and C—H···O hydrogen bonds and Cl···O contacts were found, and in LEQXOX, C—H···N and Cl···Cl contacts are observed.

#### 5. Synthesis and crystallization

The title compound was synthesized according to the reported method (Shikhaliyev *et al.*, 2018). A 20 mL screw-neck vial was charged with DMSO (10 mL), (*E*)-4-[[2-(4-fluorophenyl)hydrazono]methyl]-*N,N*-dimethylaniline (257 mg, 1 mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl<sub>4</sub> (20 mmol, 10 equiv). After 1–3 h (until TLC analysis showed complete consumption of the corresponding Schiff base), the reaction mixture was

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>16</sub> H <sub>14</sub> Cl <sub>2</sub> FN <sub>3</sub>
<i>M<sub>r</sub></i>	338.20
Crystal system, space group	Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0730 (3), 15.9782 (9), 16.3860 (7)
<i>V</i> (Å <sup>3</sup> )	1590.03 (14)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm <sup>−1</sup> )	0.42
Crystal size (mm)	0.27 × 0.24 × 0.17
Data collection	
Diffractometer	Bruker APEXII PHOTON 100 detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2003)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.887, 0.944
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	12082, 3215, 2696
<i>R<sub>int</sub></i>	0.036
(sin θ/λ) <sub>max</sub> (Å <sup>−1</sup> )	0.625
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.034, 0.084, 1.05
No. of reflections	3215
No. of parameters	201
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>−3</sup> )	0.13, −0.22
Absolute structure	Flack <i>x</i> determined using 1002 quotients [( <i>I</i> <sup>+</sup> ) − ( <i>I</i> <sup>−</sup> )] / [( <i>I</i> <sup>+</sup> ) + ( <i>I</i> <sup>−</sup> )] (Parsons <i>et al.</i> , 2013).
Absolute structure parameter	−0.02 (2)

Computer programs: *APEX3* and *SAINT* (Bruker, 2007), *SHELXT2016/6* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

poured into ~0.01 *M* solution of HCl (100 mL, pH = 2–3), and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 50 mL), brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* using a rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3/1–1/1). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution. Orange solid (78%); m.p. 418 K. Analysis calculated for C<sub>16</sub>H<sub>14</sub>Cl<sub>2</sub>FN<sub>3</sub> (*M* = 338.21): C 56.82, H 4.17, N 12.42; found: C 56.78, H 4.11, N 12.34%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 3.05 (6H, NMe<sub>2</sub>), 6.79–7.86 (8H, Ar). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm) 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, 40.31. ESI–MS: *m/z*: 338.12 [*M*+H]<sup>+</sup>.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All C-bound H atoms were refined using a riding model with *d*(C–H) = 0.93 Å, *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for aromatic and 0.96 Å, *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl H atoms.

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of 4-{2,2-dichloro-1-[(E)-(4-fluorophenyl)diazenyl]ethenyl}-*N,N*-dimethylaniline

Kadriye Özkaraca, Mehmet Akkurt, Namiq Q. Shikhaliyev, Ulviyya F. Askerova, Gulnar T. Suleymanova, Irada M. Shikhaliyeva and Ajaya Bhattarai

### Computing details

Data collection: *APEX3* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXT2016/6* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

### 4-{2,2-Dichloro-1-[(E)-(4-fluorophenyl)diazenyl]ethenyl}-*N,N*-dimethylaniline

#### Crystal data

$C_{16}H_{14}Cl_2FN_3$

$M_r = 338.20$

Orthorhombic,  $P2_12_12_1$

$a = 6.0730$  (3) Å

$b = 15.9782$  (9) Å

$c = 16.3860$  (7) Å

$V = 1590.03$  (14) Å<sup>3</sup>

$Z = 4$

$F(000) = 696$

$D_x = 1.413$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 6056 reflections

$\theta = 2.8$ – $26.4^\circ$

$\mu = 0.42$  mm<sup>-1</sup>

$T = 296$  K

Block, orange

$0.27 \times 0.24 \times 0.17$  mm

#### Data collection

Bruker APEXII PHOTON 100 detector  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2003)

$T_{\min} = 0.887$ ,  $T_{\max} = 0.944$

12082 measured reflections

3215 independent reflections

2696 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\max} = 26.4^\circ$ ,  $\theta_{\min} = 2.5^\circ$

$h = -7 \rightarrow 7$

$k = -19 \rightarrow 19$

$l = -20 \rightarrow 20$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.084$

$S = 1.05$

3215 reflections

201 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.1514P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.13$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

1002 quotients  $[(I^+) - (I^-)] / [(I^+) + (I^-)]$  (Parsons *et al.*, 2013).

Absolute structure parameter:  $-0.02$  (2)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4252 (4)	0.61833 (16)	0.56623 (16)	0.0443 (6)
C2	0.5620 (5)	0.68715 (18)	0.55987 (18)	0.0509 (7)
H2A	0.540332	0.725536	0.517976	0.061*
C3	0.7298 (5)	0.6994 (2)	0.61488 (17)	0.0573 (8)
H3A	0.823241	0.745307	0.610610	0.069*
C4	0.7553 (5)	0.6416 (2)	0.67653 (18)	0.0594 (8)
C5	0.6205 (6)	0.5739 (2)	0.6855 (2)	0.0673 (9)
H5A	0.641740	0.536178	0.728082	0.081*
C6	0.4535 (5)	0.56267 (19)	0.63053 (18)	0.0574 (8)
H6A	0.358152	0.517491	0.636245	0.069*
C7	-0.0179 (4)	0.53364 (16)	0.45205 (16)	0.0439 (6)
C8	-0.0207 (4)	0.58320 (16)	0.37493 (15)	0.0421 (6)
C9	-0.1979 (4)	0.63333 (18)	0.35356 (16)	0.0465 (6)
H9A	-0.319781	0.635689	0.387856	0.056*
C10	-0.1976 (4)	0.67976 (18)	0.28261 (16)	0.0470 (7)
H10A	-0.319254	0.712725	0.270104	0.056*
C11	-0.0185 (4)	0.67833 (17)	0.22914 (15)	0.0419 (6)
C12	0.1597 (5)	0.62650 (17)	0.25034 (16)	0.0463 (6)
H12A	0.280540	0.622891	0.215669	0.056*
C13	0.1577 (5)	0.58098 (17)	0.32175 (17)	0.0473 (6)
H13A	0.278742	0.547916	0.334730	0.057*
C14	-0.1613 (5)	0.47174 (16)	0.46824 (16)	0.0469 (6)
C15	-0.1744 (6)	0.7909 (2)	0.14541 (19)	0.0624 (8)
H15A	-0.174793	0.828007	0.191458	0.094*
H15B	-0.318008	0.766689	0.138916	0.094*
H15C	-0.136230	0.821563	0.097069	0.094*
C16	0.1532 (6)	0.7139 (2)	0.09817 (19)	0.0666 (8)
H16A	0.162051	0.655738	0.083877	0.100*
H16B	0.292048	0.732038	0.119880	0.100*
H16C	0.118356	0.746158	0.050458	0.100*
Cl1	-0.16032 (15)	0.41361 (5)	0.55620 (5)	0.0677 (3)
Cl2	-0.36345 (14)	0.44180 (5)	0.40139 (5)	0.0680 (3)
F1	0.9220 (4)	0.65309 (16)	0.73030 (13)	0.0957 (8)
N1	0.2619 (4)	0.60931 (14)	0.50431 (14)	0.0477 (5)
N2	0.1433 (4)	0.54576 (14)	0.51363 (13)	0.0469 (5)
N3	-0.0159 (4)	0.72557 (16)	0.15854 (14)	0.0554 (6)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0531 (15)	0.0378 (14)	0.0420 (13)	0.0006 (11)	-0.0011 (12)	-0.0018 (11)
C2	0.0671 (18)	0.0421 (15)	0.0436 (14)	-0.0075 (13)	0.0032 (14)	0.0000 (12)
C3	0.0676 (19)	0.0562 (17)	0.0480 (16)	-0.0201 (15)	0.0029 (15)	-0.0036 (14)
C4	0.0617 (18)	0.070 (2)	0.0468 (15)	-0.0164 (16)	-0.0090 (15)	0.0004 (15)
C5	0.079 (2)	0.065 (2)	0.0583 (18)	-0.0209 (17)	-0.0234 (17)	0.0185 (15)
C6	0.0655 (18)	0.0480 (17)	0.0588 (17)	-0.0192 (15)	-0.0148 (15)	0.0152 (14)
C7	0.0430 (13)	0.0427 (14)	0.0461 (14)	0.0082 (11)	-0.0043 (12)	-0.0006 (11)
C8	0.0433 (13)	0.0398 (14)	0.0433 (13)	0.0034 (11)	-0.0052 (12)	-0.0006 (11)
C9	0.0409 (14)	0.0550 (16)	0.0436 (14)	0.0078 (12)	0.0017 (12)	-0.0020 (12)
C10	0.0421 (14)	0.0513 (15)	0.0474 (15)	0.0121 (12)	-0.0034 (13)	0.0028 (12)
C11	0.0416 (14)	0.0435 (15)	0.0406 (14)	0.0010 (11)	-0.0047 (12)	-0.0043 (11)
C12	0.0384 (13)	0.0517 (15)	0.0486 (14)	0.0059 (12)	0.0035 (13)	-0.0033 (12)
C13	0.0392 (13)	0.0478 (14)	0.0547 (15)	0.0077 (12)	-0.0061 (13)	-0.0012 (12)
C14	0.0453 (14)	0.0438 (14)	0.0515 (14)	0.0037 (12)	-0.0048 (13)	-0.0001 (11)
C15	0.0624 (19)	0.0655 (19)	0.0591 (18)	0.0090 (16)	-0.0018 (17)	0.0153 (15)
C16	0.0647 (19)	0.075 (2)	0.0595 (18)	0.0020 (18)	0.0144 (18)	0.0095 (16)
Cl1	0.0720 (5)	0.0627 (5)	0.0683 (5)	-0.0060 (4)	0.0004 (5)	0.0197 (4)
Cl2	0.0576 (4)	0.0620 (5)	0.0845 (5)	-0.0089 (4)	-0.0209 (4)	0.0044 (4)
F1	0.0914 (16)	0.1181 (18)	0.0777 (13)	-0.0488 (14)	-0.0399 (12)	0.0172 (13)
N1	0.0566 (14)	0.0415 (12)	0.0450 (12)	-0.0009 (11)	-0.0058 (11)	0.0018 (10)
N2	0.0506 (12)	0.0449 (12)	0.0454 (11)	-0.0031 (11)	-0.0081 (11)	0.0016 (10)
N3	0.0568 (15)	0.0634 (16)	0.0461 (12)	0.0129 (12)	0.0076 (12)	0.0089 (11)

*Geometric parameters (Å, °)*

C1—C2	1.382 (4)	C10—C11	1.397 (4)
C1—C6	1.389 (4)	C10—H10A	0.9300
C1—N1	1.426 (3)	C11—N3	1.381 (3)
C2—C3	1.374 (4)	C11—C12	1.406 (4)
C2—H2A	0.9300	C12—C13	1.378 (4)
C3—C4	1.377 (4)	C12—H12A	0.9300
C3—H3A	0.9300	C13—H13A	0.9300
C4—F1	1.354 (3)	C14—Cl2	1.713 (3)
C4—C5	1.365 (4)	C14—Cl1	1.715 (3)
C5—C6	1.369 (4)	C15—N3	1.436 (4)
C5—H5A	0.9300	C15—H15A	0.9600
C6—H6A	0.9300	C15—H15B	0.9600
C7—C14	1.344 (4)	C15—H15C	0.9600
C7—N2	1.419 (3)	C16—N3	1.438 (4)
C7—C8	1.491 (4)	C16—H16A	0.9600
C8—C9	1.387 (4)	C16—H16B	0.9600
C8—C13	1.391 (4)	C16—H16C	0.9600
C9—C10	1.379 (4)	N1—N2	1.255 (3)
C9—H9A	0.9300		



C2—C1—C6	119.5 (3)	N3—C11—C10	121.7 (2)
C2—C1—N1	116.4 (2)	N3—C11—C12	121.3 (2)
C6—C1—N1	124.1 (2)	C10—C11—C12	117.0 (2)
C3—C2—C1	120.6 (3)	C13—C12—C11	120.9 (3)
C3—C2—H2A	119.7	C13—C12—H12A	119.5
C1—C2—H2A	119.7	C11—C12—H12A	119.5
C2—C3—C4	118.0 (3)	C12—C13—C8	121.7 (2)
C2—C3—H3A	121.0	C12—C13—H13A	119.1
C4—C3—H3A	121.0	C8—C13—H13A	119.1
F1—C4—C5	119.0 (3)	C7—C14—C12	122.9 (2)
F1—C4—C3	118.1 (3)	C7—C14—C11	124.2 (2)
C5—C4—C3	122.9 (3)	C12—C14—C11	112.87 (16)
C4—C5—C6	118.5 (3)	N3—C15—H15A	109.5
C4—C5—H5A	120.8	N3—C15—H15B	109.5
C6—C5—H5A	120.8	H15A—C15—H15B	109.5
C5—C6—C1	120.5 (3)	N3—C15—H15C	109.5
C5—C6—H6A	119.8	H15A—C15—H15C	109.5
C1—C6—H6A	119.8	H15B—C15—H15C	109.5
C14—C7—N2	114.0 (2)	N3—C16—H16A	109.5
C14—C7—C8	123.4 (2)	N3—C16—H16B	109.5
N2—C7—C8	122.5 (2)	H16A—C16—H16B	109.5
C9—C8—C13	117.5 (2)	N3—C16—H16C	109.5
C9—C8—C7	122.0 (2)	H16A—C16—H16C	109.5
C13—C8—C7	120.6 (2)	H16B—C16—H16C	109.5
C10—C9—C8	121.5 (3)	N2—N1—C1	113.2 (2)
C10—C9—H9A	119.2	N1—N2—C7	114.8 (2)
C8—C9—H9A	119.2	C11—N3—C15	121.0 (2)
C9—C10—C11	121.4 (2)	C11—N3—C16	120.9 (2)
C9—C10—H10A	119.3	C15—N3—C16	118.0 (2)
C11—C10—H10A	119.3		
C6—C1—C2—C3	2.2 (4)	N3—C11—C12—C13	178.6 (3)
N1—C1—C2—C3	-177.5 (2)	C10—C11—C12—C13	-1.4 (4)
C1—C2—C3—C4	-0.6 (4)	C11—C12—C13—C8	1.1 (4)
C2—C3—C4—F1	179.3 (3)	C9—C8—C13—C12	-0.1 (4)
C2—C3—C4—C5	-0.7 (5)	C7—C8—C13—C12	-179.7 (3)
F1—C4—C5—C6	-179.6 (3)	N2—C7—C14—C12	-177.0 (2)
C3—C4—C5—C6	0.4 (6)	C8—C7—C14—C12	0.6 (4)
C4—C5—C6—C1	1.2 (5)	N2—C7—C14—C11	2.1 (3)
C2—C1—C6—C5	-2.5 (5)	C8—C7—C14—C11	179.6 (2)
N1—C1—C6—C5	177.1 (3)	C2—C1—N1—N2	-179.9 (2)
C14—C7—C8—C9	63.2 (4)	C6—C1—N1—N2	0.4 (4)
N2—C7—C8—C9	-119.4 (3)	C1—N1—N2—C7	-178.6 (2)
C14—C7—C8—C13	-117.3 (3)	C14—C7—N2—N1	-172.0 (2)
N2—C7—C8—C13	60.1 (3)	C8—C7—N2—N1	10.4 (3)
C13—C8—C9—C10	-0.4 (4)	C10—C11—N3—C15	13.1 (4)
C7—C8—C9—C10	179.1 (3)	C12—C11—N3—C15	-166.9 (3)
C8—C9—C10—C11	0.0 (4)	C10—C11—N3—C16	-170.4 (3)

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C9—C10—C11—N3	-179.1 (3)	C12—C11—N3—C16	9.6 (4)
C9—C10—C11—C12	0.9 (4)		

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*Hydrogen-bond geometry (Å, °)*

Cg1 is the centroid of the C1–C6 ring.

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<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C14—C11···Cg1 <sup>i</sup>	1.72 (1)	3.93 (1)	3.882 (3)	76 (1)

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Symmetry code: (i)  $x-1, y, z$ .