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# Crystal structures and Hirshfeld surface analyses of the two isotopic compounds (*E*)-1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene

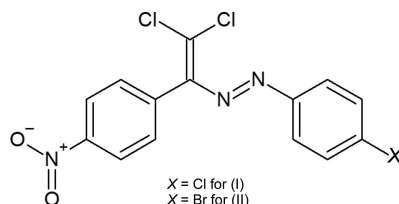
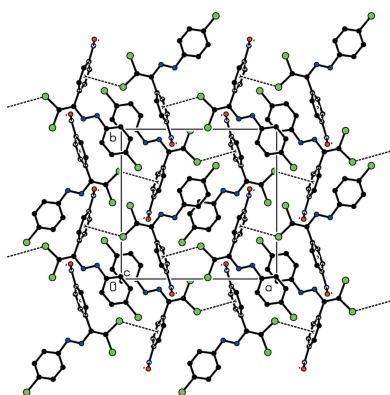
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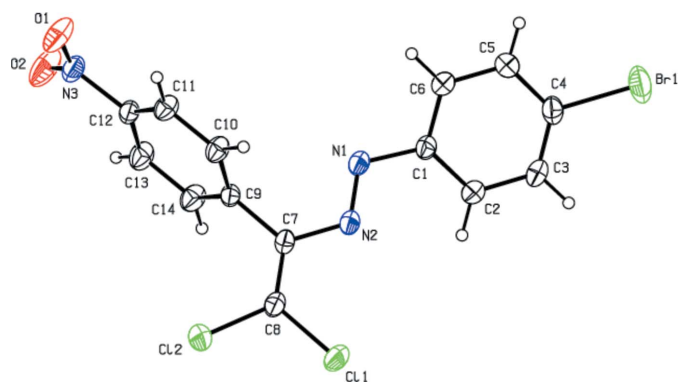
In the two isotopic title compounds, C<sub>14</sub>H<sub>8</sub>BrCl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>, (**I**), and C<sub>14</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>, (**II**), the substitution of one of the phenyl rings is different [Br for (**I**) and Cl for (**II**)]. Aromatic rings form dihedral angles of 60.9 (2) and 64.1 (2)°, respectively. Molecules are linked through weak X··Cl contacts [X = Br for (**I**) and Cl for (**II**)], 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. Hirshfeld surface analysis of the crystal structures indicates that the most important contributions for the crystal packing for (**I**) are from C··H/H··C (16.1%), O··H/H··O (13.1%), Cl··H/H··Cl (12.7%), H··H (11.4%), Br··H/H··Br (8.9%), N··H/H··N (6.9%) and Cl··C/C··Cl (6.6%) interactions, and for (**II**), from Cl··H / H··Cl (21.9%), C··H/H··C (15.3%), O··H/H··O (13.4%), H··H (11.5%), Cl··C/C··Cl (8.3%), N··H/H··N (7.0%) and Cl··Cl (5.9%) interactions. The crystal of (**I**) studied was refined as an inversion twin, the ratio of components being 0.9917 (12):0.0083 (12).

## 1. Chemical context

Compounds with azo/hydrazone moieties are ubiquitous in various fields, ranging from organic/inorganic synthesis, catalysis, and medicinal chemistry to material chemistry. They are used as dyes, ligands, solvatochromic materials, molecular switches, or analytical reagents amongst other applications (Akbari *et al.*, 2017; Asadov *et al.*, 2016; Gurbanov *et al.*, 2018; Kopylovich *et al.*, 2011; Ma *et al.*, 2017; Mahmoudi *et al.*, 2018; Mahmudov *et al.*, 2014, 2019).



The non-covalent donor/acceptor properties of azo/hydrazones depend strongly on the attached functional groups (Shikhaliyev *et al.*, 2013, 2014, 2018). In a previous study we have attached halogen atoms to dye molecules, which led to halogen bonding (Maharramov *et al.*, 2018; Shikhaliyev *et al.*,

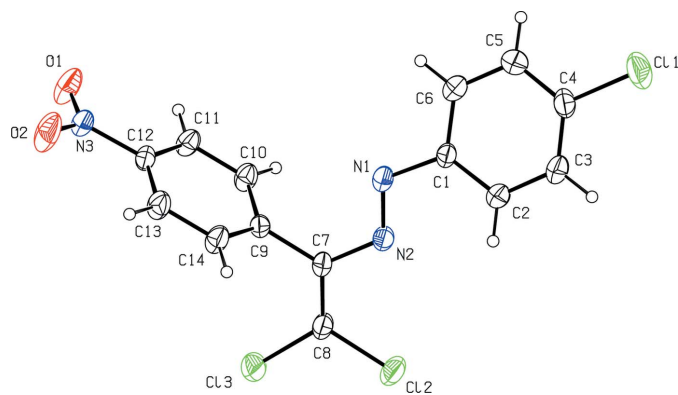


**Figure 1**  
The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

2018). In a continuation of our work in this direction, we have now synthesized two new azo dyes, (*E*)-1-(4-bromophenyl)-2-(2,2-dichloro-1-(4-nitrophenyl)vinyl)diazene (I) and (*E*)-1-(4-chlorophenyl)-2-(2,2-dichloro-1-(4-nitrophenyl)vinyl)diazene (II), and report here their molecular and crystal structures.

## 2. Structural commentary

Compounds (I) and (II) are isotypic. Their molecular structures (Figs. 1 and 2) are not planar. For the bromo-substituted compound (I), the dihedral angle between the essentially planar 4-bromophenyl ring C1–C6 [maximum deviation = 0.015 (6) Å at atom C5] and the nitro-substituted benzene ring C9–C14 [maximum deviation = –0.009 (4) Å at atom C9] is 60.9 (2)°, for the chloro-substituted compound (II) the corresponding value is 64.1 (2)°. The torsion angles involving the central diazene group amount to 18.3 (6)° for C2–C1–N1–N2, –179.1 (3)° for C1–N1–N2–C7, and 175.4 (4)° for N1–N2–C7–C8 for (I). The corresponding values for (II) are –17.0 (5)°, 179.0 (3)° and 175.4 (4)°, respectively. The bond lengths and angles are within normal ranges and are comparable to those in the related structures detailed in the *Database survey*.



**Figure 2**  
The molecular structure of (II) with displacement ellipsoids drawn at the 30% probability level.

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

Cg2 is the centroid of the C9–C14 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>
C6–H6...Cl2 <sup>i</sup>	0.93	2.92	3.593 (5)	131
C8–Cl2...Cg2 <sup>ii</sup>	1.71 (1)	3.66 (1)	4.710 (5)	118 (1)

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ; (ii)  $x - \frac{1}{2}, -y + \frac{3}{2}, z$ .

**Table 2**  
C–Cl... $\pi$  geometry (Å, °) for (II).

Cg2 is the centroid of the C9–C14 ring.

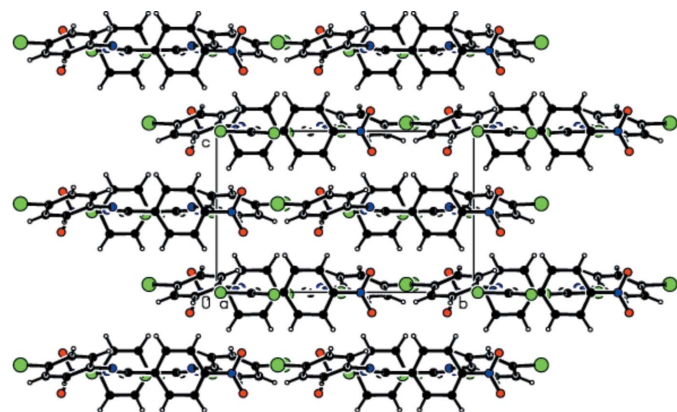
C–C... $\pi$	C–Cl	Cl... $\pi$	C... $\pi$	C–C... $\pi$
C8–Cl3...Cg2 <sup>i</sup>	1.71 (1)	3.62 (1)	4.703 (3)	120 (1)

Symmetry code: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ .

## 3. Supramolecular features and Hirshfeld surface analysis

As a result of the isotypism of (I) and (II), the packing features are generally very similar in the two structures. Molecules are linked by weak Br...Cl contacts [for (I)] or Cl...Cl contacts [for (II)] and C–H...Cl interactions into chains extending along the *a*-axis direction (Tables 1–3; Figs. 3 and 4). Additional C–Cl... $\pi$  interactions lead to the formation of sheets parallel to the *ab* plane (Fig. 5). van der Waals interactions (Table 3) consolidate the three-dimensional packing.

Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was used to investigate the intermolecular interactions in the crystal structures of both compounds (*CrystalExplorer3.1*; Wolff *et al.*, 2012). The surface plots (Spackman *et al.*, 2008) mapped over  $d_{\text{norm}}$  were generated to quantify and visualize the intermolecular interactions and to explain the observed crystal packing. Dark-red spots on the  $d_{\text{norm}}$  surface arise as a result of short interatomic contacts (Tables 1–3), while the other weaker intermolecular interactions appear as light-red spots.



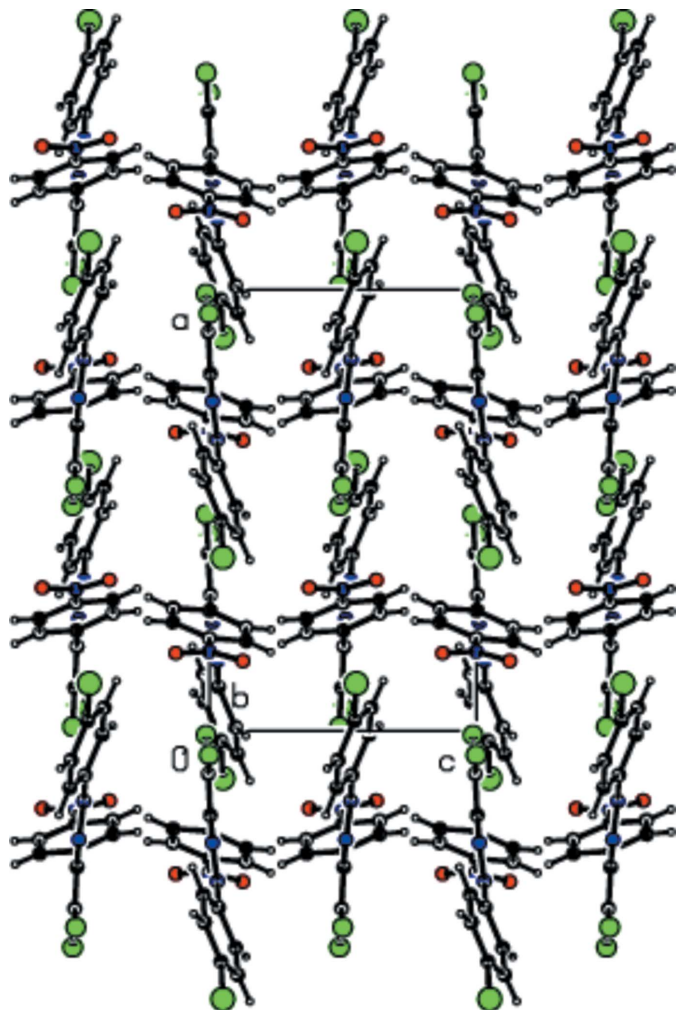
**Figure 3**  
Packing in the crystal structure of (I) showing chains running parallel to the *a*-axis.

**Table 3**

Summary of short interatomic contacts (Å) in the crystal structures of compounds (I) and (II).

Contact	Distance	Symmetry operation
Compound (I)		
H10...Br1	3.18	$1 - x, 1 - y, \frac{1}{2} + z$
Br1...Cl1	3.5125 (12)	$\frac{1}{2} + x, \frac{1}{2} - y, z$
H2...H11	2.54	$\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$
Cl2...H6	2.92	$-\frac{1}{2} + x, \frac{1}{2} - y, z$
O2...H3	2.68	$x, 1 + y, z$
H13...N2	2.73	$\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$
Compound (II)		
H10...Cl1	3.13	$2 - x, -y, -\frac{1}{2} + z$
Cl1...Cl2	3.4847 (14)	$\frac{1}{2} + x, -\frac{1}{2} - y, z$
H2...H11	2.56	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$
Cl3...H6	2.98	$-\frac{1}{2} + x, \frac{1}{2} - y, z$
O2...H3	2.66	$x, 1 + y, z$
H13...N2	2.69	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

For (I), the red points, which represent closer contacts and negative  $d_{\text{norm}}$  values on the surface, correspond to the C—H...O interactions. The reciprocal O...H/H...O interactions appear as two symmetrical broad wings in the two-dimensional fingerprint plots with  $d_e + d_i \approx 2.5$  Å and contribute


**Figure 4**  
 A view of the packing in (I) along the *a* axis showing C—H...Cl contacts.

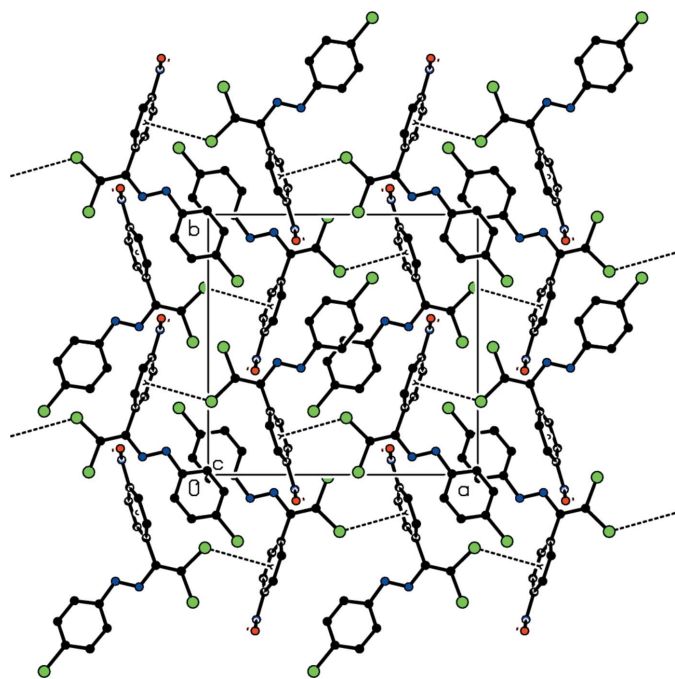
**Table 4**

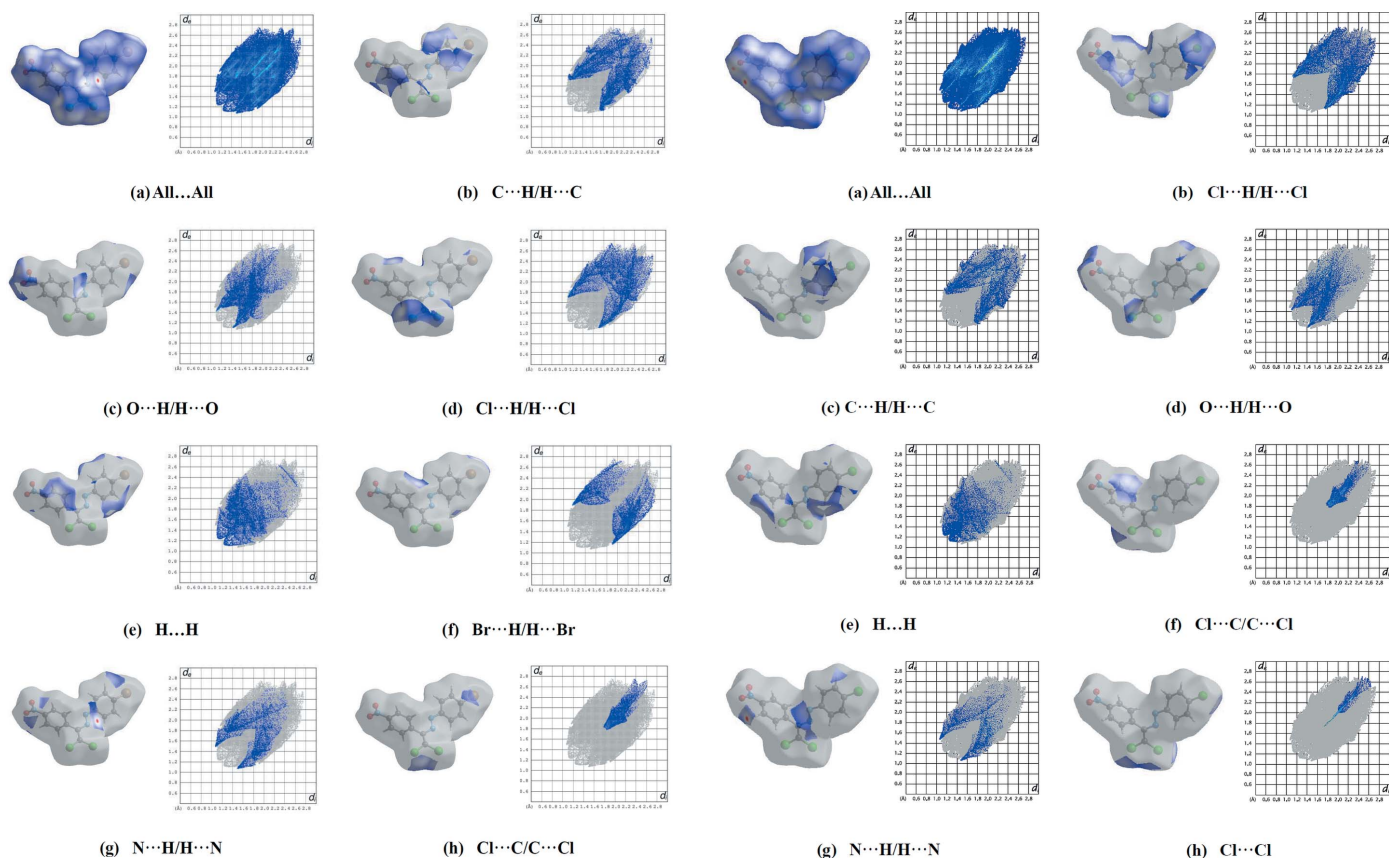
Percentage contributions of interatomic contacts to the Hirshfeld surface in the crystal structures of compounds (I) and (II).

Contact	(I)	(II)
C...H/H...C	16.1	15.3
O...H/H...O	13.1	13.4
Cl...H/H...Cl	12.7	21.9
H...H	11.4	11.5
Br...H/H...Br	8.9	—
N...H/H...N	6.9	7.0
Cl...C/C...Cl	6.6	8.3
Cl...Br/Br...Cl	5.2	—
Cl...O/O...Cl	4.9	5.8
O...C/C...O	3.8	3.9
Cl...N/N...Cl	3.4	3.4
C...C	2.1	2.3
Br...C/C...Br	1.5	—
Br...O/O...Br	1.2	—
N...O/O...N	1.1	1.0
Cl...Cl	1.0	5.9
N...C/C...N	0.1	0.2
Br...N/N...Br	0.1	—

13.1% to the Hirshfeld surface (Fig. 6b). The reciprocal Cl...H/H...Cl interaction with a contribution of 13.8% is present as sharp symmetrical spikes at  $d_e + d_i \approx 2.8$  Å (Fig. 6c).

For (II), the percentage contributions of various contacts to the total Hirshfeld surface are shown in the two-dimensional fingerprint plots in Fig. 7. The reciprocal Cl...H/H...Cl interactions appear as two symmetrical broad wings with  $d_e + d_i \approx 2.9$  Å and contribute 21.9% to the Hirshfeld surface (Fig. 7b). The reciprocal C...H/H...C and O...H/H...O interactions (15.3, 13.4% contributions, respectively) are present as sharp symmetrical spikes at  $d_e + d_i \approx 2.95$  and 2.5 Å, respectively (Fig. 7c–d). The small percentage contri-


**Figure 5**  
 Formation of sheets in (II) parallel to *ab* through C—Cl... $\pi$  contacts.

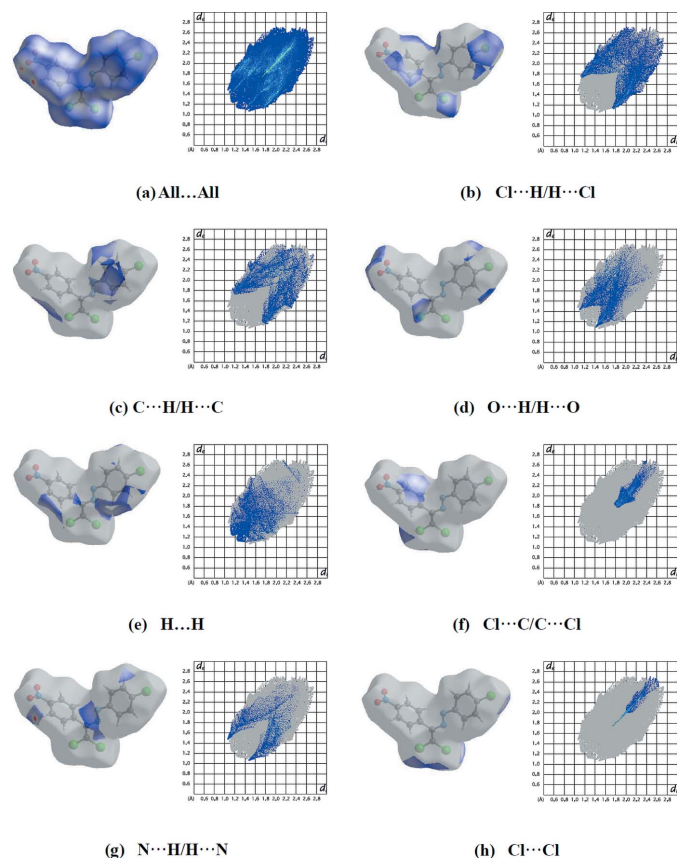


**Figure 6**  
Hirshfeld surface representations and full two-dimensional fingerprint plots for (I), showing (a) all interactions, and delineated into (b) C...H/H...C (c), O...H/H...O (d), Cl...H/H...Cl (e), H...H (f), Br...H/H...Br (g), N...H/H...N and (h) Cl...C/C...Cl interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from a given point on the Hirshfeld surface.

Contributions of both compounds to the Hirshfeld surfaces from the various other interatomic contacts are comparatively listed in Table 4. Although there is almost agreement on the values given for the molecules of (I) and (II), some differences are due to the different halogen atoms substituting the phenyl ring and the different molecular environment in the crystal structures.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, November 2018; Groom *et al.*, 2016) for structures having an (*E*)-1-(2,2-dichloro-1-phenylvinyl)-2-phenyldiazene unit gave 23 hits. Four compounds closely resemble the title compound, *viz.* 1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-fluorophenyl)ethenyl]diazene (CSD refcode 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-



**Figure 7**  
The Hirshfeld surface representations and the full two-dimensional fingerprint plots for (II), showing (a) all interactions, and delineated into (b) Cl...H/H...Cl, (c) C...H/H...C, (d) O...H/H...O, (e) H...H, (f) Cl...C/C...Cl, (g) N...H/H...N and (h) Cl...Cl interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in Å) from a given point on the Hirshfeld surface.

(4-chlorophenyl)ethenyl]diazene} (LEQXOX; Shikhaliyev *et al.*, 2018),

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  $\pi$ – $\pi$  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... $\pi$ , C—F... $\pi$  and N—O... $\pi$  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

Dyes (I) and (II) were synthesized according to a literature protocol (Shikhaliyev *et al.*, 2018). For (I), a 20 ml screw neck vial was charged with DMSO (10 ml), (*E*)-1-(4-bromophenyl)-2-(4-nitrobenzylidene)hydrazine (320 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

**Table 5**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C <sub>14</sub> H <sub>8</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>8</sub> Cl <sub>3</sub> N <sub>3</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	401.04	356.58
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.9181 (7), 13.4336 (6), 8.4080 (4)	13.8689 (7), 13.3674 (7), 8.3620 (5)
<i>V</i> (Å <sup>3</sup> )	1572.05 (13)	1550.24 (15)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	2.96	0.60
Crystal size (mm)	0.19 × 0.14 × 0.08	0.17 × 0.14 × 0.07
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2003)	Multi-scan ( <i>SADABS</i> ; Bruker, 2003)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.608, 0.784	0.911, 0.946
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	23012, 3429, 2811	11687, 3156, 2547
<i>R<sub>int</sub></i>	0.057	0.038
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.641	0.626
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>	0.033, 0.081, 1.02	0.037, 0.091, 1.04
No. of reflections	3429	3156
No. of parameters	200	199
No. of restraints	1	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.31, -0.50	0.18, -0.25
Absolute structure	Refined as an inversion twin	Flack <i>x</i> determined using 1011 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	0.008 (13)	0.14 (3)

Computer programs: *APEX3* and *SAINT* (Bruker, 2007), *SHELXT2016/6* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(until TLC analysis showed complete consumption of the corresponding Schiff base), the reaction mixture was poured into 0.01 *M* solution of HCl (100 ml, pH ~2-3), and extracted with dichloromethane (3 × 20 ml). The organic phases were combined and washed with water (3 × 50 ml), brine (30 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* in a rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (*v/v*: 3/1–1/1). An orange solid was obtained (yield 58%); mp 418 K. Analysis calculated for C<sub>14</sub>H<sub>8</sub>BrCl<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (*M* = 401.04): C, 41.93; H, 2.01; N, 10.48; found: C, 41.87; H, 2.03; N, 10.39%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.30 (*d*, 2H, *J* = 9.02 Hz), 7.65–7.56 (*m*, 4H), 7.38 (*d*, 2H, *J* = 9.24 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 151.26, 150.60, 147.97, 139.21, 137.18, 132.49, 131.28, 126.83, 124.72, 123.44. ESI-MS: *m/z*: 402.08 [*M* + H]<sup>+</sup>.

For (II), the procedure was the same as that for (I) using (*E*)-1-(4-chlorophenyl)-2-(4-nitrobenzylidene)hydrazine (276 mg, 1 mmol). An orange solid was obtained (yield 64%); mp 448 K. Analysis calculated for C<sub>14</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub> (*M* = 356.59): C, 47.16; H, 2.26; N, 11.78; found: C, 47.09; H, 2.23; N, 11.65%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.32–7.37 (8H, Ar). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.91, 150.55, 147.98, 139.28, 138.22, 137.02, 131.24, 129.49, 124.52, 123.44. ESI-MS: *m/z*: 357.70 [*M* + H]<sup>+</sup>.

Compounds (I) and (II) were dissolved in dichloromethane and then left at room temperature for slow evaporation;

orange crystals of both compounds suitable for X-rays started to form after *ca* 2 d.

## 6. Refinement

Crystal data collection and structure refinement details are summarized in Table 5. C-bound H atoms were constrained to ideal values with C–H = 0.93 Å and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). The crystal of (I) studied was refined as an inversion twin, the ratio of components being 0.9917 (12):0.0083 (12).

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## supporting information

*Acta Cryst.* (2019). E75, 1199-1204 [https://doi.org/10.1107/S2056989019010004]

## Crystal structures and Hirshfeld surface analyses of the two isotypic compounds (*E*)-1-(4-bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene and (*E*)-1-(4-chlorophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene

Mehmet Akkurt, Namiq Q. Shikhaliyev, Gulnar T. Suleymanova, Gulnare V. Babayeva, Gunay Z. Mammadova, Ayten A. Niyazova, Irada M. Shikhaliyeva and Flavien A. A. Toze

### Computing details

For both structures, data collection: *APEX3* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (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, 2009).

### (*E*)-1-(4-Bromophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (I)

#### Crystal data

$C_{14}H_8BrCl_2N_3O_2$

$M_r = 401.04$

Orthorhombic, *Pna*2<sub>1</sub>

$a = 13.9181$  (7) Å

$b = 13.4336$  (6) Å

$c = 8.4080$  (4) Å

$V = 1572.05$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 792$

$D_x = 1.694$  Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8656 reflections

$\theta = 2.9\text{--}27.0^\circ$

$\mu = 2.96$  mm<sup>-1</sup>

$T = 296$  K

Plate, orange

0.19 × 0.14 × 0.08 mm

#### Data collection

Bruker APEXII CCD

diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

$T_{\min} = 0.608$ ,  $T_{\max} = 0.784$

23012 measured reflections

3429 independent reflections

2811 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 27.1^\circ$ ,  $\theta_{\min} = 2.9^\circ$

$h = -17 \rightarrow 17$

$k = -14 \rightarrow 17$

$l = -10 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.081$

$S = 1.02$

3429 reflections

200 parameters

1 restraint

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 0.7719P]$

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

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

$\Delta\rho_{\max} = 0.31$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.50$  e Å<sup>-3</sup>

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.008 (13)

*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.

**Refinement.** Refined as a 2-component inversion twin.

*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	0.4004 (2)	0.5082 (3)	0.5333 (5)	0.0393 (8)
C2	0.3711 (3)	0.4164 (3)	0.4764 (6)	0.0478 (10)
H2	0.309463	0.408665	0.435584	0.057*
C3	0.4334 (3)	0.3360 (3)	0.4803 (6)	0.0545 (11)
H3	0.414420	0.274430	0.440786	0.065*
C4	0.5228 (3)	0.3483 (3)	0.5428 (6)	0.0481 (9)
C5	0.5526 (3)	0.4381 (4)	0.6048 (7)	0.0582 (13)
H5	0.613115	0.444124	0.650896	0.070*
C6	0.4915 (3)	0.5191 (3)	0.5976 (6)	0.0539 (12)
H6	0.511337	0.580727	0.635893	0.065*
C7	0.1912 (2)	0.6569 (2)	0.5030 (5)	0.0378 (8)
C8	0.0975 (3)	0.6351 (3)	0.4948 (6)	0.0477 (10)
C9	0.2272 (3)	0.7616 (2)	0.5010 (5)	0.0345 (7)
C10	0.2658 (3)	0.8034 (3)	0.6372 (5)	0.0437 (9)
H10	0.270870	0.765504	0.729433	0.052*
C11	0.2966 (3)	0.9009 (3)	0.6369 (5)	0.0442 (9)
H11	0.321785	0.929565	0.728509	0.053*
C12	0.2896 (2)	0.9547 (3)	0.4988 (5)	0.0374 (8)
C13	0.2538 (4)	0.9149 (3)	0.3622 (5)	0.0511 (11)
H13	0.250600	0.952658	0.269651	0.061*
C14	0.2221 (3)	0.8170 (3)	0.3637 (5)	0.0491 (10)
H14	0.197279	0.788772	0.271406	0.059*
N1	0.3411 (2)	0.5954 (2)	0.5291 (5)	0.0427 (7)
N2	0.2537 (2)	0.5747 (2)	0.5107 (4)	0.0403 (7)
N3	0.3201 (2)	1.0595 (2)	0.4987 (5)	0.0483 (8)
O1	0.3418 (3)	1.0978 (3)	0.6245 (5)	0.0769 (11)
O2	0.3240 (4)	1.1036 (3)	0.3734 (5)	0.0863 (14)
Cl1	0.05489 (8)	0.51572 (8)	0.4988 (2)	0.0743 (4)
Cl2	0.00955 (8)	0.72322 (9)	0.4870 (2)	0.0713 (4)
Br1	0.60741 (4)	0.23804 (4)	0.54965 (11)	0.0809 (2)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0435 (18)	0.0297 (16)	0.045 (2)	0.0001 (13)	0.0007 (18)	0.0047 (18)
C2	0.045 (2)	0.038 (2)	0.060 (3)	-0.0022 (16)	-0.0050 (19)	-0.007 (2)
C3	0.060 (3)	0.0298 (19)	0.074 (3)	-0.0012 (17)	-0.002 (2)	-0.006 (2)



C4	0.051 (2)	0.0365 (18)	0.057 (3)	0.0094 (15)	0.006 (2)	0.008 (2)
C5	0.043 (2)	0.046 (3)	0.085 (4)	0.0025 (18)	-0.010 (2)	0.002 (2)
C6	0.048 (2)	0.036 (2)	0.077 (3)	-0.0035 (16)	-0.011 (2)	-0.003 (2)
C7	0.0440 (18)	0.0276 (15)	0.042 (2)	0.0021 (14)	0.0025 (17)	0.0016 (16)
C8	0.046 (2)	0.0290 (18)	0.068 (3)	-0.0009 (14)	0.005 (2)	-0.0031 (18)
C9	0.0358 (17)	0.0277 (16)	0.0399 (19)	0.0020 (12)	0.0015 (15)	0.0014 (16)
C10	0.058 (3)	0.035 (2)	0.038 (2)	-0.0045 (18)	-0.0006 (18)	0.0050 (17)
C11	0.056 (2)	0.038 (2)	0.039 (2)	-0.0060 (18)	-0.0025 (18)	-0.0039 (17)
C12	0.0395 (17)	0.0273 (16)	0.045 (2)	0.0006 (13)	0.0045 (17)	0.0003 (17)
C13	0.069 (3)	0.039 (2)	0.046 (2)	-0.004 (2)	-0.006 (2)	0.0098 (18)
C14	0.065 (3)	0.041 (2)	0.041 (2)	-0.007 (2)	-0.009 (2)	0.0037 (18)
N1	0.0446 (16)	0.0288 (14)	0.055 (2)	-0.0015 (11)	0.0023 (16)	0.0018 (15)
N2	0.0437 (15)	0.0280 (13)	0.0493 (19)	0.0012 (12)	0.0009 (15)	0.0017 (14)
N3	0.0564 (19)	0.0302 (16)	0.058 (2)	-0.0046 (14)	0.0018 (19)	0.0012 (18)
O1	0.119 (3)	0.041 (2)	0.071 (2)	-0.022 (2)	-0.004 (2)	-0.0088 (18)
O2	0.142 (4)	0.044 (2)	0.074 (3)	-0.028 (2)	-0.011 (2)	0.0190 (19)
Cl1	0.0508 (6)	0.0360 (5)	0.1362 (12)	-0.0104 (4)	0.0112 (8)	-0.0047 (7)
Cl2	0.0438 (5)	0.0440 (6)	0.1260 (13)	0.0068 (4)	0.0004 (7)	-0.0025 (7)
Br1	0.0781 (3)	0.0554 (3)	0.1093 (5)	0.0306 (2)	0.0097 (4)	0.0087 (4)

*Geometric parameters (Å, °)*

C1—C2	1.384 (5)	C8—C11	1.710 (4)
C1—C6	1.385 (6)	C9—C14	1.376 (6)
C1—N1	1.434 (4)	C9—C10	1.384 (6)
C2—C3	1.386 (6)	C10—C11	1.378 (6)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.361 (6)	C11—C12	1.371 (6)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.377 (6)	C12—C13	1.361 (6)
C4—Br1	1.893 (4)	C12—N3	1.470 (4)
C5—C6	1.384 (6)	C13—C14	1.387 (6)
C5—H5	0.9300	C13—H13	0.9300
C6—H6	0.9300	C14—H14	0.9300
C7—C8	1.338 (5)	N1—N2	1.257 (4)
C7—N2	1.407 (4)	N3—O2	1.209 (5)
C7—C9	1.493 (4)	N3—O1	1.214 (5)
C8—Cl2	1.705 (4)		
C2—C1—C6	120.0 (4)	C14—C9—C10	119.7 (3)
C2—C1—N1	123.3 (3)	C14—C9—C7	120.1 (3)
C6—C1—N1	116.7 (3)	C10—C9—C7	120.2 (3)
C1—C2—C3	120.1 (4)	C11—C10—C9	120.3 (4)
C1—C2—H2	120.0	C11—C10—H10	119.8
C3—C2—H2	120.0	C9—C10—H10	119.8
C4—C3—C2	119.1 (4)	C12—C11—C10	118.7 (4)
C4—C3—H3	120.4	C12—C11—H11	120.6
C2—C3—H3	120.4	C10—C11—H11	120.6

C3—C4—C5	121.9 (4)	C13—C12—C11	122.2 (3)
C3—C4—Br1	119.0 (3)	C13—C12—N3	118.8 (4)
C5—C4—Br1	119.1 (3)	C11—C12—N3	119.0 (4)
C4—C5—C6	119.1 (4)	C12—C13—C14	118.8 (4)
C4—C5—H5	120.4	C12—C13—H13	120.6
C6—C5—H5	120.4	C14—C13—H13	120.6
C5—C6—C1	119.8 (4)	C9—C14—C13	120.3 (4)
C5—C6—H6	120.1	C9—C14—H14	119.9
C1—C6—H6	120.1	C13—C14—H14	119.9
C8—C7—N2	115.7 (3)	N2—N1—C1	112.3 (3)
C8—C7—C9	122.2 (3)	N1—N2—C7	115.5 (3)
N2—C7—C9	122.2 (3)	O2—N3—O1	122.7 (3)
C7—C8—C12	123.3 (3)	O2—N3—C12	118.8 (4)
C7—C8—C11	122.8 (3)	O1—N3—C12	118.5 (4)
C12—C8—C11	113.8 (2)		
C6—C1—C2—C3	-1.5 (7)	C7—C9—C10—C11	-178.3 (4)
N1—C1—C2—C3	178.2 (4)	C9—C10—C11—C12	-0.9 (7)
C1—C2—C3—C4	1.0 (7)	C10—C11—C12—C13	-0.4 (7)
C2—C3—C4—C5	1.1 (8)	C10—C11—C12—N3	178.4 (4)
C2—C3—C4—Br1	179.5 (4)	C11—C12—C13—C14	1.0 (7)
C3—C4—C5—C6	-2.7 (8)	N3—C12—C13—C14	-177.9 (4)
Br1—C4—C5—C6	179.0 (4)	C10—C9—C14—C13	-1.2 (7)
C4—C5—C6—C1	2.1 (8)	C7—C9—C14—C13	178.8 (4)
C2—C1—C6—C5	0.0 (7)	C12—C13—C14—C9	-0.1 (7)
N1—C1—C6—C5	-179.8 (4)	C2—C1—N1—N2	18.3 (6)
N2—C7—C8—C12	179.2 (3)	C6—C1—N1—N2	-161.9 (4)
C9—C7—C8—C12	-1.9 (7)	C1—N1—N2—C7	-179.1 (3)
N2—C7—C8—C11	1.8 (6)	C8—C7—N2—N1	-175.4 (4)
C9—C7—C8—C11	-179.4 (3)	C9—C7—N2—N1	5.7 (5)
C8—C7—C9—C14	-70.7 (6)	C13—C12—N3—O2	-9.3 (6)
N2—C7—C9—C14	108.1 (5)	C11—C12—N3—O2	171.8 (5)
C8—C7—C9—C10	109.3 (5)	C13—C12—N3—O1	171.9 (5)
N2—C7—C9—C10	-71.9 (5)	C11—C12—N3—O1	-7.0 (6)
C14—C9—C10—C11	1.7 (7)		

*Hydrogen-bond geometry (Å, °)*

Cg2 is the centroid of the C9—C14 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>
C6—H6...C12 <sup>i</sup>	0.93	2.92	3.593 (5)	131
C8—C12...Cg2 <sup>ii</sup>	1.71 (1)	3.66 (1)	4.710 (5)	118 (1)

Symmetry codes: (i)  $x+1/2, -y+3/2, z$ ; (ii)  $x-1/2, -y+3/2, z$ .

**(E)-1-(4-Chlorophenyl)-2-[2,2-dichloro-1-(4-nitrophenyl)ethenyl]diazene (II)***Crystal data*C<sub>14</sub>H<sub>8</sub>Cl<sub>3</sub>N<sub>3</sub>O<sub>2</sub>M<sub>r</sub> = 356.58Orthorhombic, *Pna*2<sub>1</sub>

a = 13.8689 (7) Å

b = 13.3674 (7) Å

c = 8.3620 (5) Å

V = 1550.24 (15) Å<sup>3</sup>

Z = 4

F(000) = 720

D<sub>x</sub> = 1.528 Mg m<sup>-3</sup>

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 4206 reflections

θ = 2.9–26.4°

μ = 0.60 mm<sup>-1</sup>

T = 296 K

Prisme, orange

0.17 × 0.14 × 0.07 mm

*Data collection*

Bruker APEXII CCD

diffractometer

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

T<sub>min</sub> = 0.911, T<sub>max</sub> = 0.946

11687 measured reflections

3156 independent reflections

2547 reflections with I &gt; 2σ(I)

R<sub>int</sub> = 0.038θ<sub>max</sub> = 26.4°, θ<sub>min</sub> = 2.9°

h = -17→16

k = -16→15

l = -10→10

*Refinement*Refinement on F<sup>2</sup>

Least-squares matrix: full

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.037wR(F<sup>2</sup>) = 0.091

S = 1.04

3156 reflections

199 parameters

1 restraint

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0419P)<sup>2</sup> + 0.3296P]where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3(Δ/σ)<sub>max</sub> < 0.001Δρ<sub>max</sub> = 0.18 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0.25 e Å<sup>-3</sup>

Absolute structure: Flack x determined using

1011 quotients [(I<sup>+</sup>)-(I<sup>-</sup>)]/[(I<sup>+</sup>)+(I<sup>-</sup>)] (Parsons *et al.*, 2013).

Absolute structure parameter: 0.14 (3)

*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 (Å<sup>2</sup>)*

	x	y	z	U <sub>iso</sub> */U <sub>eq</sub>
C1	0.9044 (2)	0.0035 (2)	0.3115 (4)	0.0400 (8)
C2	0.8753 (3)	-0.0900 (2)	0.3650 (5)	0.0507 (9)
H2	0.813001	-0.099076	0.403349	0.061*
C3	0.9385 (3)	-0.1694 (2)	0.3615 (6)	0.0569 (10)
H3	0.919592	-0.231831	0.399107	0.068*
C4	1.0294 (3)	-0.1555 (3)	0.3023 (5)	0.0532 (10)
C5	1.0584 (3)	-0.0645 (3)	0.2434 (6)	0.0646 (12)
H5	1.119552	-0.056954	0.199546	0.077*
C6	0.9962 (3)	0.0155 (3)	0.2498 (6)	0.0607 (11)
H6	1.015836	0.077758	0.212526	0.073*

C7	0.6941 (2)	0.1515 (2)	0.3415 (4)	0.0376 (7)
C8	0.6001 (2)	0.1294 (2)	0.3491 (6)	0.0480 (8)
C9	0.7299 (2)	0.2569 (2)	0.3447 (5)	0.0364 (6)
C10	0.7644 (3)	0.3003 (3)	0.2053 (4)	0.0464 (9)
H10	0.766518	0.263150	0.111319	0.056*
C11	0.7955 (3)	0.3983 (3)	0.2056 (4)	0.0461 (9)
H11	0.818819	0.427923	0.112661	0.055*
C12	0.7913 (2)	0.4511 (2)	0.3468 (5)	0.0386 (7)
C13	0.7591 (3)	0.4093 (3)	0.4853 (5)	0.0530 (10)
H13	0.757981	0.446192	0.579602	0.064*
C14	0.7280 (3)	0.3110 (3)	0.4834 (5)	0.0507 (10)
H14	0.705639	0.281565	0.577118	0.061*
N1	0.8441 (2)	0.09023 (19)	0.3159 (4)	0.0446 (7)
N2	0.75630 (18)	0.06882 (17)	0.3339 (4)	0.0408 (6)
N3	0.8211 (2)	0.55693 (19)	0.3468 (5)	0.0487 (7)
O1	0.8400 (3)	0.5963 (2)	0.2197 (4)	0.0754 (10)
O2	0.8259 (3)	0.6004 (2)	0.4729 (4)	0.0879 (13)
Cl1	1.10869 (9)	-0.25630 (8)	0.2991 (2)	0.0857 (4)
Cl2	0.55690 (6)	0.00980 (6)	0.3445 (2)	0.0727 (3)
Cl3	0.51218 (7)	0.21874 (7)	0.3590 (2)	0.0751 (4)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0437 (17)	0.0277 (14)	0.048 (2)	-0.0013 (12)	-0.0011 (15)	-0.0030 (14)
C2	0.0481 (18)	0.0381 (16)	0.066 (2)	-0.0012 (14)	0.008 (2)	0.008 (2)
C3	0.062 (2)	0.0325 (16)	0.076 (3)	-0.0010 (15)	0.003 (2)	0.007 (2)
C4	0.053 (2)	0.0379 (18)	0.069 (3)	0.0094 (15)	-0.0048 (18)	-0.0087 (18)
C5	0.046 (2)	0.054 (2)	0.093 (3)	0.0019 (18)	0.012 (2)	0.001 (2)
C6	0.052 (2)	0.039 (2)	0.091 (3)	-0.0075 (17)	0.008 (2)	0.004 (2)
C7	0.0461 (16)	0.0271 (13)	0.0397 (17)	0.0000 (12)	-0.0005 (18)	-0.0028 (17)
C8	0.0471 (17)	0.0284 (14)	0.069 (2)	-0.0008 (13)	-0.004 (2)	0.0006 (19)
C9	0.0361 (14)	0.0294 (13)	0.0437 (17)	0.0023 (11)	-0.0006 (16)	-0.0014 (19)
C10	0.065 (2)	0.037 (2)	0.037 (2)	-0.0058 (17)	0.0002 (18)	-0.0045 (16)
C11	0.061 (2)	0.038 (2)	0.039 (2)	-0.0090 (17)	0.0010 (17)	0.0031 (16)
C12	0.0427 (16)	0.0273 (13)	0.0458 (18)	-0.0003 (12)	-0.0036 (19)	-0.0010 (19)
C13	0.075 (3)	0.039 (2)	0.046 (2)	-0.0076 (19)	0.0109 (19)	-0.0099 (17)
C14	0.073 (3)	0.037 (2)	0.042 (2)	-0.0102 (18)	0.0089 (19)	-0.0038 (17)
N1	0.0476 (15)	0.0295 (12)	0.057 (2)	-0.0009 (11)	0.0003 (14)	-0.0009 (14)
N2	0.0427 (14)	0.0313 (12)	0.0485 (16)	-0.0006 (10)	-0.0025 (15)	-0.0011 (15)
N3	0.0533 (16)	0.0323 (13)	0.061 (2)	-0.0051 (12)	0.001 (2)	0.002 (2)
O1	0.118 (3)	0.0418 (17)	0.067 (2)	-0.0227 (18)	0.0012 (19)	0.0106 (17)
O2	0.149 (4)	0.0453 (19)	0.069 (2)	-0.028 (2)	0.013 (2)	-0.0211 (18)
Cl1	0.0767 (7)	0.0574 (6)	0.1230 (12)	0.0296 (5)	-0.0039 (7)	-0.0084 (7)
Cl2	0.0513 (5)	0.0375 (4)	0.1292 (10)	-0.0109 (3)	-0.0096 (7)	0.0036 (7)
Cl3	0.0456 (5)	0.0450 (5)	0.1348 (11)	0.0067 (4)	-0.0006 (7)	0.0016 (7)

*Geometric parameters (Å, °)*

C1—C6	1.383 (5)	C8—C13	1.708 (3)
C1—C2	1.387 (5)	C9—C14	1.368 (5)
C1—N1	1.430 (4)	C9—C10	1.387 (5)
C2—C3	1.377 (5)	C10—C11	1.379 (5)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.366 (6)	C11—C12	1.377 (5)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.373 (6)	C12—C13	1.362 (6)
C4—C11	1.740 (4)	C12—N3	1.473 (4)
C5—C6	1.374 (6)	C13—C14	1.382 (5)
C5—H5	0.9300	C13—H13	0.9300
C6—H6	0.9300	C14—H14	0.9300
C7—C8	1.339 (4)	N1—N2	1.259 (4)
C7—N2	1.404 (4)	N3—O2	1.207 (5)
C7—C9	1.493 (4)	N3—O1	1.214 (4)
C8—C12	1.708 (3)		
C6—C1—C2	119.5 (3)	C14—C9—C10	119.9 (3)
C6—C1—N1	117.0 (3)	C14—C9—C7	120.5 (3)
C2—C1—N1	123.5 (3)	C10—C9—C7	119.6 (3)
C3—C2—C1	120.2 (3)	C11—C10—C9	120.3 (3)
C3—C2—H2	119.9	C11—C10—H10	119.9
C1—C2—H2	119.9	C9—C10—H10	119.9
C4—C3—C2	119.4 (3)	C12—C11—C10	118.4 (3)
C4—C3—H3	120.3	C12—C11—H11	120.8
C2—C3—H3	120.3	C10—C11—H11	120.8
C3—C4—C5	121.3 (3)	C13—C12—C11	122.2 (3)
C3—C4—C11	118.9 (3)	C13—C12—N3	119.1 (3)
C5—C4—C11	119.7 (3)	C11—C12—N3	118.7 (3)
C4—C5—C6	119.4 (4)	C12—C13—C14	118.9 (3)
C4—C5—H5	120.3	C12—C13—H13	120.6
C6—C5—H5	120.3	C14—C13—H13	120.6
C5—C6—C1	120.2 (4)	C9—C14—C13	120.4 (4)
C5—C6—H6	119.9	C9—C14—H14	119.8
C1—C6—H6	119.9	C13—C14—H14	119.8
C8—C7—N2	115.3 (3)	N2—N1—C1	112.6 (2)
C8—C7—C9	122.1 (3)	N1—N2—C7	114.9 (2)
N2—C7—C9	122.7 (3)	O2—N3—O1	123.0 (3)
C7—C8—C12	123.2 (2)	O2—N3—C12	118.5 (3)
C7—C8—C13	122.9 (2)	O1—N3—C12	118.4 (3)
C12—C8—C13	113.90 (19)		
C6—C1—C2—C3	2.1 (7)	C7—C9—C10—C11	178.5 (3)
N1—C1—C2—C3	-178.0 (4)	C9—C10—C11—C12	0.0 (6)
C1—C2—C3—C4	-1.1 (7)	C10—C11—C12—C13	1.1 (6)
C2—C3—C4—C5	-1.3 (7)	C10—C11—C12—N3	-177.8 (3)

C2—C3—C4—C11	179.8 (3)	C11—C12—C13—C14	-1.1 (6)
C3—C4—C5—C6	2.6 (8)	N3—C12—C13—C14	177.7 (3)
C11—C4—C5—C6	-178.5 (4)	C10—C9—C14—C13	0.9 (6)
C4—C5—C6—C1	-1.6 (8)	C7—C9—C14—C13	-178.5 (4)
C2—C1—C6—C5	-0.8 (7)	C12—C13—C14—C9	0.1 (6)
N1—C1—C6—C5	179.4 (4)	C6—C1—N1—N2	162.9 (4)
N2—C7—C8—C12	-1.8 (6)	C2—C1—N1—N2	-17.0 (5)
C9—C7—C8—C12	179.6 (3)	C1—N1—N2—C7	179.0 (3)
N2—C7—C8—C13	-179.9 (3)	C8—C7—N2—N1	175.4 (4)
C9—C7—C8—C13	1.4 (6)	C9—C7—N2—N1	-5.9 (5)
C8—C7—C9—C14	73.1 (5)	C13—C12—N3—O2	7.8 (5)
N2—C7—C9—C14	-105.4 (4)	C11—C12—N3—O2	-173.3 (4)
C8—C7—C9—C10	-106.3 (5)	C13—C12—N3—O1	-172.4 (4)
N2—C7—C9—C10	75.2 (5)	C11—C12—N3—O1	6.5 (5)
C14—C9—C10—C11	-0.9 (6)		

*Hydrogen-bond geometry (Å, °)*

Cg2 is the centroid of the C9—C14 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>
C8—C13...Cg2 <sup>i</sup>	1.71 (1)	3.62 (1)	4.703 (3)	120 (1)

Symmetry code: (i)  $x-1/2, -y+1/2, z$ .