



# Crystal structure and Hirshfeld surface analysis of (*E*)-2-(4-bromophenyl)-1-[2,2-dibromo-1-(4-nitrophenyl)ethenyl]diazene

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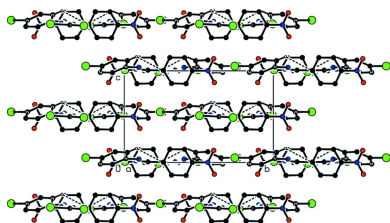
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The molecule of the title compound, C<sub>14</sub>H<sub>8</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>2</sub>, consists of three almost planar groups: the central dibromoethenyldiazene fragment and two attached aromatic rings. The mean planes of these rings form dihedral angles with the plane of the central fragment of 26.35 (15) and 72.57 (14)° for bromine- and nitro-substituted rings, respectively. In the crystal, C—H...Br interactions connect molecules, generating zigzag C(8) chains along the [100] direction. These chains are linked by C—Br...π interactions into layers parallel to (001). van der Waals interactions between the layers aid in the cohesion of the crystal packing. The most substantial contributions to crystal packing, according to a Hirshfeld surface analysis, are from Br...H/H...Br (20.9%), C...H/H...C (15.2%), O...H/H...O (12.6%) and H...H (11.7%) contacts.

## 1. Chemical context

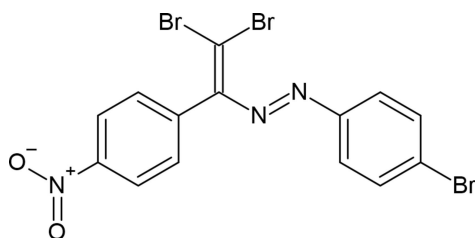
Azo dyes constitute the largest production volume (*ca* 70%) of the dye industry today, and their relative importance may increase further in the future (Lipskikh *et al.*, 2018). They play a crucial role in the printing market, the design of functional materials attributed to smart hydrogen bonding, photo-triggered structural switching, self-assembled layers, ionophores, liquid crystals, semiconductors, indicators, spectrophotometric reagents for determination of metal ions, photoluminescent materials, catalysts, antimicrobial agents, optical recording media, spin-coating films, *etc* (Zollinger, 1994, 1995; Gurbanov *et al.*, 2020*a,b*; Mahmudov *et al.*, 2010, 2013). Depending on the attached substituents, the functional properties of azo compounds and their metal complexes can be improved/controlled (Ma *et al.*, 2020, 2021). Both *E/Z* isomerism and azo-hydrazo tautomerism properties of azo dyes are key phenomena in the synthesis and development of new functional materials (Shikhaliyev *et al.*, 2018, 2019). The attachment of non-covalent bond acceptor or donor centres to the azo dyes can be used as a synthetic strategy for the improvement of the functional properties of their metal complexes (Mahmudov *et al.*, 2020, 2021, 2022). Thus, we have attached bromine atoms and a nitro group together with aryl rings to the —N=N— linkage leading to a new azo compound, (*E*)-2-(4-bromophenyl)-1-[2,2-dibromo-1-(4-nitrophenyl)ethenyl]di-



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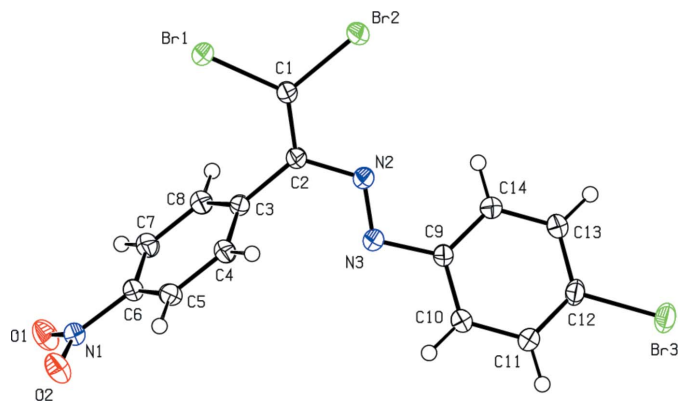
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azene, which can provide intermolecular halogen and hydrogen bonds as well as  $\pi$ -interactions.

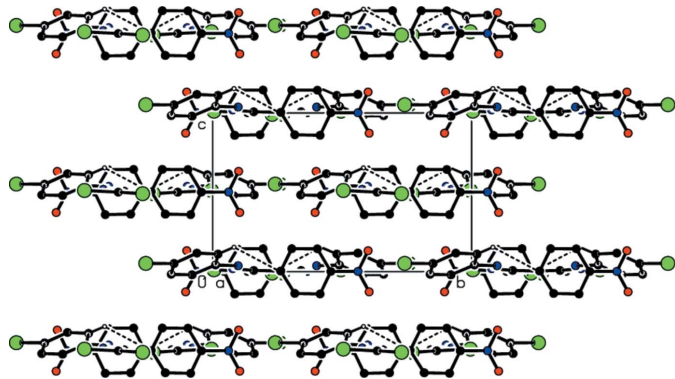


## 2. Structural commentary

The molecule of the title compound (Fig. 1) consists of three almost planar groups: the central dibromoethenyldiazene fragment [largest deviation from the l.s. plane is 0.039 (3) Å for N2] and two attached aromatic rings. The mean planes of these rings form dihedral angles with the plane of the central fragment of 26.35 (15) and 72.57 (14)° for the bromine- and nitro-substituted rings, respectively. The nitro group is twisted by 8.1 (2)° with respect to the C3–C8 aromatic ring. The C2–N2 bond distance of 1.406 (4) Å indicates  $\pi$ -conjugation between ethene and diazo groups. All other bond lengths and angles in the title compound are similar to those reported for



**Figure 1**  
The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
View down the *a*-axis of the title compound showing the C–H...Br interactions.

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

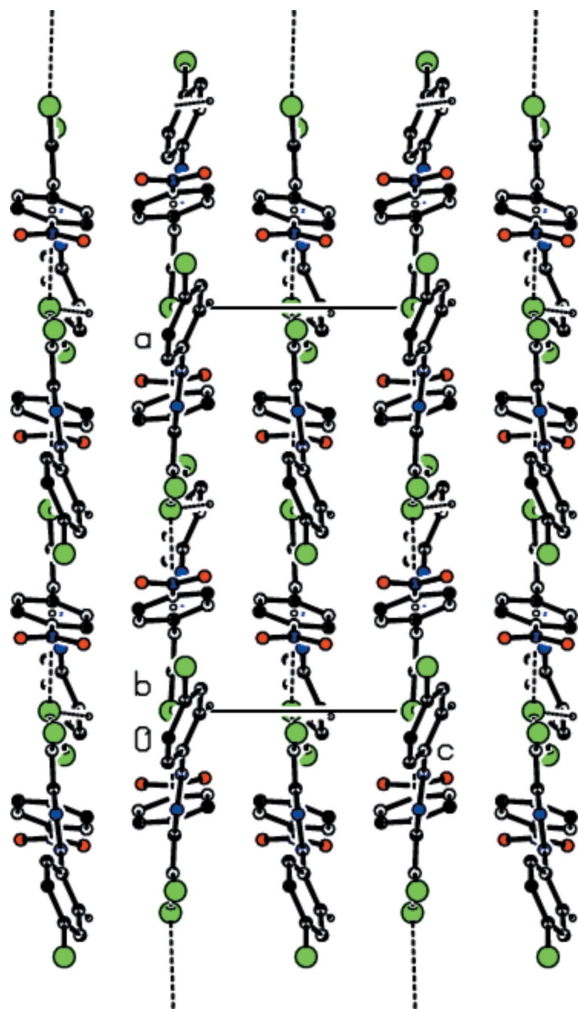
<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C10–H10...Br1 <sup>i</sup>	0.95	2.89	3.530 (4)	126

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

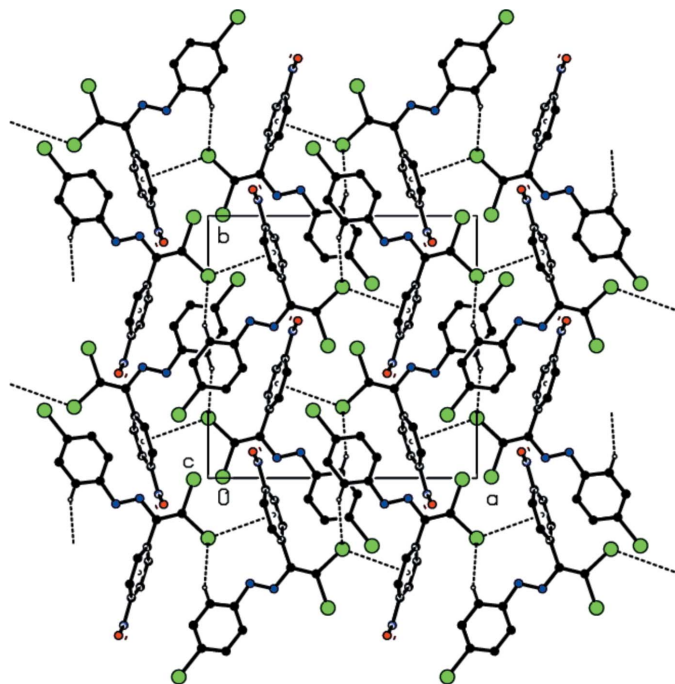
the related azo compounds discussed in the *Database survey* section.

## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, C–H...Br interactions connect the molecules, generating zigzag *C*(8) chains (Bernstein *et al.*, 1995) along the [100] direction (Table 1, Figs. 2 and 3). These chains are linked by C–Br... $\pi$  interactions [C1–Br1...Cg1<sup>ii</sup>; C1–Br1 = 1.864 (3) Å, Br1...Cg1<sup>ii</sup> = 3.5803 (16) Å, C1...Cg1<sup>ii</sup> = 4.722 (3) Å, C1–Br1...Cg1<sup>ii</sup> = 116.77 (9)°; Cg1 is the centroid of the C3–C8 ring; symmetry code (ii):  $x + \frac{1}{2}, -y + \frac{3}{2}, z$ ] into



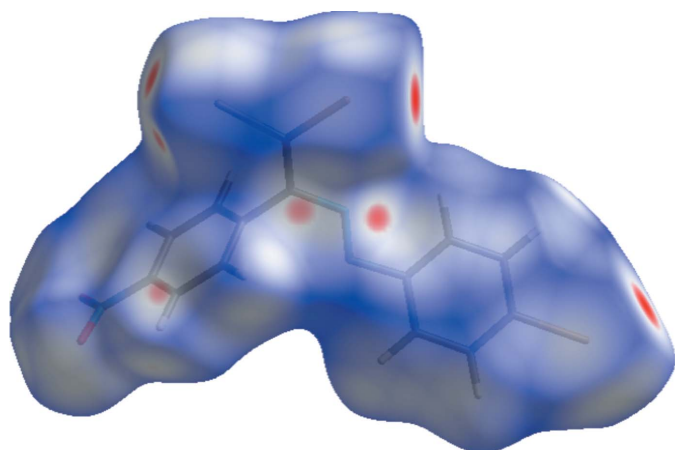
**Figure 3**  
View down the *b*-axis of the title compound, showing the C–Br... $\pi$  interactions.



**Figure 4**  
View down the  $c$  axis of the title compound, showing the  $C-Br \cdots \pi$  interactions.

layers parallel to (001) (Fig. 4). van der Waals interactions between the layers help to keep the crystal packing together.

*Crystal Explorer 17.5* (Turner *et al.*, 2017) was used to perform a Hirshfeld surface analysis and to generate the corresponding two-dimensional fingerprint plots, with a standard resolution of the three-dimensional  $d_{\text{norm}}$  surfaces plotted over a fixed color scale of  $-0.1401$  (red) to  $1.1158$  (blue) a.u. (Fig. 5). The red patches represent short contacts and negative  $d_{\text{norm}}$  values on the surface, which correspond to the  $C-H \cdots Br$  hydrogen bonds discussed above (Table 1). The  $C10-H10 \cdots Br1$  interactions, which are important for molecular packing of the title compound, are responsible for the red patch that appears around Br1.

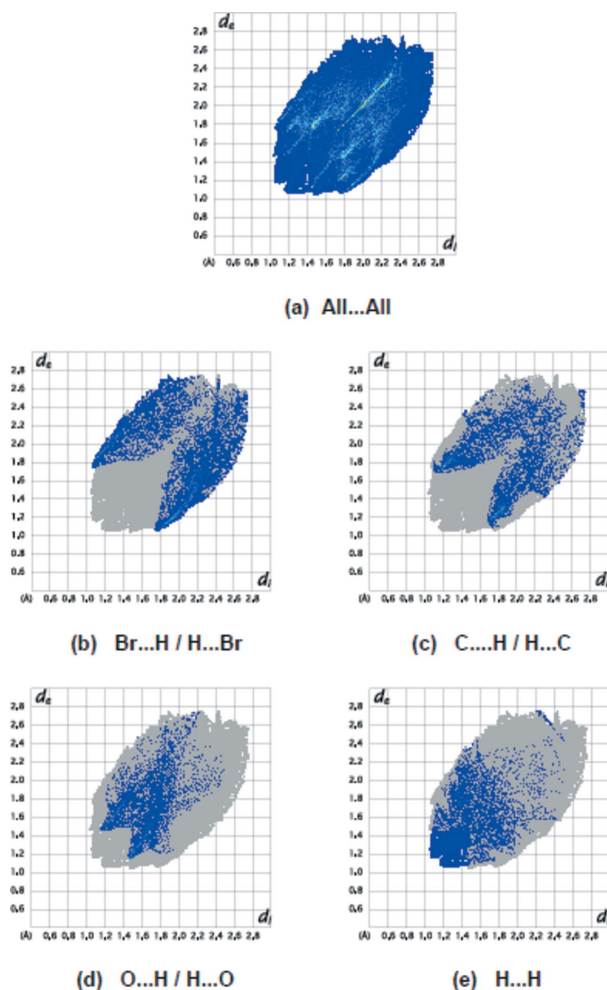


**Figure 5**  
View of the three-dimensional Hirshfeld surface of the title compound plotted over  $d_{\text{norm}}$  in the range  $-0.1401$  to  $1.1158$  a.u.

**Table 2**  
Summary of short interatomic contacts ( $\text{\AA}$ ) in the title compound.

$Br1 \cdots H10$	2.89	$\frac{1}{2} + x, \frac{3}{2} - y, z$
$H14 \cdots H5$	2.40	$\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$
$Br2 \cdots Br3$	3.44	$\frac{1}{2} + x, \frac{1}{2} - y, z$
$H10 \cdots C13$	3.02	$-x, 1 - y, \frac{1}{2} + z$
$O1 \cdots H13$	2.75	$x, 1 + y, z$
$H7 \cdots N2$	2.65	$\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$

The overall two-dimensional fingerprint plot for the title compound and those delineated into  $Br \cdots H / H \cdots Br$  (20.9%),  $C \cdots H / H \cdots C$  (15.2%),  $O \cdots H / H \cdots O$  (12.6%) and  $H \cdots H$  (11.7%) contacts are shown in Fig. 6, while numerical details for short intermolecular contacts are given in Table 2.  $Br \cdots C / C \cdots Br$  (8.8%),  $Br \cdots Br$  (6.7%),  $N \cdots H / H \cdots N$  (6.5%),  $Br \cdots O / O \cdots Br$  (5.6%),  $O \cdots C / C \cdots O$  (4.1%),  $Br \cdots N / N \cdots Br$  (3.9%),  $C \cdots C$  (2.5%),  $O \cdots N / N \cdots O$  (1.3%) and  $N \cdots C / C \cdots N$  (0.1%) contacts have little directional influence on the molecular packing.



**Figure 6**  
The full two-dimensional fingerprint plots for the title compound, showing all interactions (a) and delineated into (b)  $Br \cdots H / H \cdots Br$ , (c)  $C \cdots H / H \cdots C$ , (d)  $O \cdots H / H \cdots O$ , and (e)  $H \cdots H$  interactions. The  $d_i$  and  $d_e$  values are the closest internal and external distances (in  $\text{\AA}$ ) from given points on the Hirshfeld surface.

#### 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) for similar structures with the (*E*)-1-(2,2-dibromo-1-phenylethenyl)-2-phenyldiazene fragment showed that the nine closest are those of CSD refcodes TAZDIL [(**I**); Atioğlu *et al.*, 2022], PAXDOL [(**II**); Çelikesir *et al.*, 2022], GUPHIL [(**III**); Özkaraca *et al.*, 2020*b*], HONBUK [(**IV**); Akkurt *et al.*, 2019], HONBOE [(**V**); Akkurt *et al.*, 2019], HODQAV [(**VI**); Shikhaliyev *et al.*, 2019], XIZREG [(**VII**); Atioğlu *et al.*, 2019], LEQXOX [(**VIII**); Shikhaliyev *et al.*, 2018] and LEQXIR [(**IX**); Shikhaliyev *et al.*, 2018].

In (**I**), the molecules are connected by C—H···O and C—H···F hydrogen bonds into layers parallel to (011). The crystal packing is consolidated by C—Br··· $\pi$  and C—F··· $\pi$  contacts, as well as by  $\pi$ – $\pi$  stacking interactions. In the crystal of (**II**), the molecules are linked into chains running parallel to [001] by C—H···O hydrogen bonds. The crystal packing is consolidated by C—F··· $\pi$  contacts and  $\pi$ – $\pi$  stacking interactions, and short Br···O [2.9828 (13) Å] distances are also observed. In the crystal of (**III**), the molecules are linked into inversion dimers *via* short halogen–halogen contacts [Cl1···Cl1 = 3.3763 (9) Å, Cl16—Cl1···Cl1 = 141.47 (7)°] compared to the van der Waals radius sum of 3.50 Å for two chlorine atoms. No other directional contacts could be identified, and the shortest aromatic ring centroid separation is greater than 5.25 Å. In the crystals of (**IV**) and (**V**), the molecules are linked through weak X···Cl contacts [X = Cl for (**IV**) and Br for (**V**)], C—H···Cl and C—Cl··· $\pi$  interactions into sheets lying parallel to (001). In the crystal of (**VI**), the molecules are stacked in columns parallel to [100] *via* weak C—H···Cl hydrogen bonds and face-to-face  $\pi$ – $\pi$  stacking interactions. The crystal packing is further consolidated by short Cl···Cl contacts. In (**VII**), molecules are linked by C—H···O hydrogen bonds into zigzag chains running parallel to [001]. The crystal packing also features C—Cl··· $\pi$ , C—F··· $\pi$  and N—O··· $\pi$  interactions. In (**VIII**), C—H···N and short Cl···Cl contacts are observed, and in (**IX**), C—H···N and C—H···O hydrogen bonds and short Cl···O contacts occur.

#### 5. Synthesis and crystallization

This dye was synthesized according to the reported method (Akkurt *et al.*, 2019; Atioğlu *et al.*, 2019; Maharramov *et al.*, 2018; Özkaraca *et al.*, 2020*a,b*). A 20 mL screw neck vial was charged with DMSO (10 mL), (*E*)-1-(4-bromophenyl)-2-(4-nitrobenzylidene)hydrazine (1 mmol), tetramethylethylenediamine (TMEDA; 295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CBr<sub>4</sub> (4.5 mmol). After 1–3 h (until TLC analysis showed complete consumption of 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 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

Table 3

Experimental details.

Crystal data	
Chemical formula	C <sub>14</sub> H <sub>8</sub> Br <sub>3</sub> N <sub>3</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	489.96
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 <sub>1</sub>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.8678 (5), 13.5442 (5), 8.3017 (3)
<i>V</i> (Å <sup>3</sup> )	1559.29 (10)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	7.77
Crystal size (mm)	0.31 × 0.14 × 0.08
Data collection	
Diffractometer	Bruker D8 QUEST, Photon III detector
Absorption correction	Multi-scan ( <i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.044, 0.110
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	75835, 7370, 5962
<i>R<sub>int</sub></i>	0.057
(sin θ/ <i>λ</i> ) <sub>max</sub> (Å <sup>-1</sup> )	0.826
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, 0.085, 1.02
No. of reflections	7370
No. of parameters	199
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	1.41, -0.97
Absolute structure	Flack parameter determined using 2437 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	0.003 (5)

Computer programs: *APEX3* and *SAINT* (Bruker, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

graphy 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. Red solid (58%); m.p. 398 K. Analysis calculated for C<sub>14</sub>H<sub>8</sub>Br<sub>3</sub>N<sub>3</sub>O<sub>2</sub> (*M* = 489.95): C 34.32, H 1.65, N 8.58; found: C 34.27, H 1.70, N 8.56%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16–7.41 (8H, Ar–H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 150.89, 149.62, 148.26, 136.43, 132.25, 127.77, 125.57, 124.53, 123.57, 93.24. ESI–MS: *m/z*: 490.96 [*M* + H]<sup>+</sup>.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically and constrained to ride on their parent atoms (C—H = 0.95 Å) with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C). One reflection (110), affected by the beam stop, was omitted in the final cycles of refinement.

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The authors' contributions are as follows. Conceptualization, NQS, MA and AB; synthesis, NAM and GTS; X-ray analysis, SÖY, VNK and MA; writing (review and editing of the

manuscript) SÖY, MA and AB; funding acquisition, NQS, NAM and GTS; supervision, NQS, MA and AB.

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of (*E*)-2-(4-bromophenyl)-1-[2,2-dibromo-1-(4-nitrophenyl)ethenyl]diazene

Mehmet Akkurt, Sema Öztürk Yıldırım, Namiq Q. Shikhaliyev, Naila A. Mammadova, Ayten A. Niyazova, Victor N. Khrustalev and Ajaya Bhattarai

### Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINT* (Bruker, 2018); data reduction: *SAINT* (Bruker, 2018); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

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

#### Crystal data

$C_{14}H_8Br_3N_3O_2$

$M_r = 489.96$

Orthorhombic, *Pna2<sub>1</sub>*

$a = 13.8678$  (5) Å

$b = 13.5442$  (5) Å

$c = 8.3017$  (3) Å

$V = 1559.29$  (10) Å<sup>3</sup>

$Z = 4$

$F(000) = 936$

$D_x = 2.087$  Mg m<sup>-3</sup>

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

Cell parameters from 9976 reflections

$\theta = 2.9$ – $34.8^\circ$

$\mu = 7.77$  mm<sup>-1</sup>

$T = 100$  K

Block, red

$0.31 \times 0.14 \times 0.08$  mm

#### Data collection

Bruker D8 QUEST, Photon III detector  
diffractometer

Radiation source: fine-focus sealed X-Ray tube

Graphite monochromator

Detector resolution: 7.31 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  shutterless scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.044$ ,  $T_{\max} = 0.110$

75835 measured reflections

7370 independent reflections

5962 reflections with  $I > 2\sigma(I)$

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

$\theta_{\max} = 36.0^\circ$ ,  $\theta_{\min} = 2.9^\circ$

$h = -22 \rightarrow 22$

$k = -22 \rightarrow 22$

$l = -13 \rightarrow 13$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.085$

$S = 1.02$

7370 reflections

199 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.8309P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 1.41 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.97 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack parameter determined using 2437 quotients  $[(F^+)-(F^-)]/[(F^+)+(F^-)]$  (Parsons *et al.*, 2013).

Absolute structure parameter: 0.003 (5)

### 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.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.49964 (2)	0.72932 (3)	0.49158 (6)	0.02765 (8)
Br2	0.44572 (2)	0.50470 (2)	0.51189 (7)	0.02906 (8)
Br3	-0.10955 (3)	0.24165 (3)	0.55241 (7)	0.03182 (9)
O1	0.1810 (2)	1.1045 (2)	0.3729 (4)	0.0333 (6)
O2	0.1662 (3)	1.1002 (2)	0.6323 (4)	0.0326 (6)
N1	0.18506 (19)	1.0613 (2)	0.5020 (5)	0.0231 (5)
N2	0.24431 (19)	0.57755 (19)	0.5188 (4)	0.0207 (5)
N3	0.15599 (19)	0.5982 (2)	0.5376 (4)	0.0228 (6)
C1	0.4020 (2)	0.6350 (2)	0.5012 (6)	0.0222 (6)
C2	0.3073 (2)	0.6586 (2)	0.5080 (5)	0.0205 (5)
C3	0.2727 (2)	0.7629 (2)	0.5040 (5)	0.0196 (5)
C4	0.2373 (3)	0.8055 (3)	0.6449 (5)	0.0221 (6)
H4	0.233234	0.767615	0.741062	0.027*
C5	0.2076 (3)	0.9043 (3)	0.6441 (5)	0.0222 (6)
H5	0.184039	0.934772	0.739348	0.027*
C6	0.2136 (2)	0.9563 (2)	0.5016 (5)	0.0212 (5)
C7	0.2468 (3)	0.9148 (3)	0.3596 (5)	0.0249 (7)
H7	0.248972	0.952162	0.262834	0.030*
C8	0.2769 (3)	0.8171 (3)	0.3629 (5)	0.0235 (6)
H8	0.300598	0.787169	0.267351	0.028*
C9	0.0971 (2)	0.5110 (2)	0.5422 (5)	0.0208 (6)
C10	0.0066 (3)	0.5207 (3)	0.6113 (5)	0.0251 (7)
H10	-0.013356	0.582330	0.654399	0.030*
C11	-0.0553 (3)	0.4391 (3)	0.6172 (5)	0.0262 (7)
H11	-0.117165	0.444374	0.665505	0.031*
C12	-0.0249 (3)	0.3509 (2)	0.5516 (5)	0.0243 (6)
C13	0.0662 (2)	0.3397 (2)	0.4837 (5)	0.0246 (7)
H13	0.085933	0.277960	0.440465	0.030*
C14	0.1275 (2)	0.4203 (2)	0.4803 (5)	0.0236 (6)

H14            0.190380            0.413915            0.435972            0.028\*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01833 (12)	0.02119 (13)	0.0434 (2)	-0.00217 (10)	0.00069 (14)	0.00037 (16)
Br2	0.02025 (12)	0.01897 (13)	0.0480 (2)	0.00223 (10)	-0.00256 (15)	-0.00061 (14)
Br3	0.02917 (16)	0.02402 (15)	0.0423 (2)	-0.00937 (12)	-0.00254 (18)	0.00189 (17)
O1	0.0460 (17)	0.0222 (13)	0.0317 (15)	0.0060 (12)	0.0009 (13)	0.0062 (11)
O2	0.0450 (16)	0.0217 (13)	0.0310 (16)	0.0042 (12)	0.0006 (13)	-0.0038 (11)
N1	0.0211 (10)	0.0185 (11)	0.0296 (15)	0.0000 (8)	0.0007 (13)	-0.0001 (12)
N2	0.0179 (10)	0.0190 (10)	0.0251 (15)	-0.0007 (8)	-0.0006 (10)	0.0012 (11)
N3	0.0184 (11)	0.0192 (11)	0.0306 (17)	-0.0012 (8)	0.0016 (10)	0.0014 (11)
C1	0.0181 (11)	0.0170 (11)	0.0315 (16)	0.0001 (9)	-0.0020 (13)	-0.0003 (13)
C2	0.0182 (11)	0.0171 (11)	0.0263 (15)	0.0002 (9)	-0.0010 (12)	0.0015 (12)
C3	0.0164 (10)	0.0167 (11)	0.0257 (15)	-0.0004 (8)	-0.0012 (13)	0.0022 (12)
C4	0.0237 (14)	0.0183 (13)	0.0243 (16)	0.0015 (11)	0.0002 (12)	0.0010 (12)
C5	0.0215 (14)	0.0211 (14)	0.0241 (16)	0.0024 (11)	0.0005 (12)	-0.0010 (12)
C6	0.0194 (11)	0.0166 (11)	0.0275 (15)	0.0000 (9)	-0.0004 (13)	-0.0007 (13)
C7	0.0262 (15)	0.0209 (14)	0.0276 (18)	0.0018 (12)	0.0018 (13)	0.0031 (12)
C8	0.0238 (14)	0.0202 (14)	0.0265 (17)	0.0003 (11)	0.0022 (13)	0.0003 (12)
C9	0.0189 (12)	0.0167 (11)	0.0269 (17)	-0.0010 (9)	-0.0007 (11)	0.0000 (12)
C10	0.0230 (14)	0.0182 (13)	0.0342 (19)	0.0003 (11)	0.0021 (13)	-0.0015 (13)
C11	0.0203 (13)	0.0209 (14)	0.037 (2)	-0.0021 (11)	0.0034 (13)	-0.0005 (13)
C12	0.0238 (13)	0.0185 (12)	0.0305 (17)	-0.0061 (10)	-0.0016 (13)	0.0016 (14)
C13	0.0246 (13)	0.0182 (12)	0.0312 (19)	-0.0007 (10)	0.0009 (14)	-0.0027 (13)
C14	0.0205 (12)	0.0208 (13)	0.0295 (19)	-0.0005 (10)	0.0035 (13)	-0.0024 (13)

*Geometric parameters (Å, °)*

Br1—C1	1.864 (3)	C5—H5	0.9500
Br2—C1	1.868 (3)	C6—C7	1.384 (6)
Br3—C12	1.888 (3)	C7—C8	1.388 (5)
O1—N1	1.223 (5)	C7—H7	0.9500
O2—N1	1.231 (5)	C8—H8	0.9500
N1—C6	1.477 (4)	C9—C10	1.386 (5)
N2—N3	1.266 (4)	C9—C14	1.397 (5)
N2—C2	1.406 (4)	C10—C11	1.400 (5)
N3—C9	1.437 (4)	C10—H10	0.9500
C1—C2	1.352 (4)	C11—C12	1.378 (5)
C2—C3	1.492 (4)	C11—H11	0.9500
C3—C8	1.384 (5)	C12—C13	1.392 (5)
C3—C4	1.394 (5)	C13—C14	1.384 (5)
C4—C5	1.400 (5)	C13—H13	0.9500
C4—H4	0.9500	C14—H14	0.9500
C5—C6	1.379 (5)		
O1—N1—O2	123.8 (3)	C6—C7—H7	121.0



O1—N1—C6	118.1 (3)	C8—C7—H7	121.0
O2—N1—C6	118.1 (3)	C3—C8—C7	120.7 (3)
N3—N2—C2	115.9 (3)	C3—C8—H8	119.6
N2—N3—C9	111.8 (3)	C7—C8—H8	119.6
C2—C1—Br1	123.1 (2)	C10—C9—C14	120.6 (3)
C2—C1—Br2	122.4 (2)	C10—C9—N3	116.6 (3)
Br1—C1—Br2	114.43 (15)	C14—C9—N3	122.8 (3)
C1—C2—N2	115.0 (3)	C9—C10—C11	119.7 (3)
C1—C2—C3	122.3 (3)	C9—C10—H10	120.2
N2—C2—C3	122.7 (3)	C11—C10—H10	120.2
C8—C3—C4	120.3 (3)	C12—C11—C10	118.9 (3)
C8—C3—C2	120.5 (3)	C12—C11—H11	120.6
C4—C3—C2	119.1 (3)	C10—C11—H11	120.6
C3—C4—C5	119.7 (3)	C11—C12—C13	122.1 (3)
C3—C4—H4	120.2	C11—C12—Br3	119.2 (3)
C5—C4—H4	120.2	C13—C12—Br3	118.7 (3)
C6—C5—C4	118.3 (3)	C14—C13—C12	118.7 (3)
C6—C5—H5	120.8	C14—C13—H13	120.7
C4—C5—H5	120.8	C12—C13—H13	120.7
C5—C6—C7	122.9 (3)	C13—C14—C9	120.0 (3)
C5—C6—N1	118.3 (3)	C13—C14—H14	120.0
C7—C6—N1	118.8 (3)	C9—C14—H14	120.0
C6—C7—C8	118.0 (3)		
C2—N2—N3—C9	178.1 (3)	O2—N1—C6—C7	-171.8 (3)
Br1—C1—C2—N2	-178.4 (3)	C5—C6—C7—C8	-1.2 (5)
Br2—C1—C2—N2	-1.8 (6)	N1—C6—C7—C8	177.5 (3)
Br1—C1—C2—C3	1.6 (6)	C4—C3—C8—C7	0.6 (5)
Br2—C1—C2—C3	178.2 (3)	C2—C3—C8—C7	-178.5 (3)
N3—N2—C2—C1	174.8 (4)	C6—C7—C8—C3	0.6 (5)
N3—N2—C2—C3	-5.2 (5)	N2—N3—C9—C10	160.3 (4)
C1—C2—C3—C8	72.2 (5)	N2—N3—C9—C14	-20.0 (5)
N2—C2—C3—C8	-107.7 (4)	C14—C9—C10—C11	-0.9 (6)
C1—C2—C3—C4	-106.9 (5)	N3—C9—C10—C11	178.9 (4)
N2—C2—C3—C4	73.1 (5)	C9—C10—C11—C12	-0.9 (6)
C8—C3—C4—C5	-1.3 (5)	C10—C11—C12—C13	1.7 (7)
C2—C3—C4—C5	177.8 (3)	C10—C11—C12—Br3	-177.8 (3)
C3—C4—C5—C6	0.8 (5)	C11—C12—C13—C14	-0.8 (6)
C4—C5—C6—C7	0.5 (5)	Br3—C12—C13—C14	178.8 (3)
C4—C5—C6—N1	-178.2 (3)	C12—C13—C14—C9	-1.0 (6)
O1—N1—C6—C5	-172.7 (3)	C10—C9—C14—C13	1.8 (6)
O2—N1—C6—C5	6.9 (4)	N3—C9—C14—C13	-177.9 (4)
O1—N1—C6—C7	8.6 (5)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
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C10—H10 $\cdots$ Br1 <sup>i</sup>	0.95	2.89	3.530 (4)	126
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Symmetry code: (i)  $x-1/2, -y+3/2, z$ .