



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

Sevim Türktekin Çelikesir,^a Mehmet Akkurt,^a Namiq Q. Shikhaliyev,^b Naila A. Mammadova,^b Gulnar T. Suleymanova,^b Victor N. Khrustalev^{c,d} and Ajaya Bhattarai^{e*}

Received 17 January 2022

Accepted 13 March 2022

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; C—F... π interaction; π – π stacking interaction; Hirshfeld surface analysis.

CCDC reference: 2158375

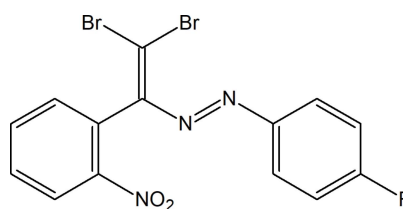
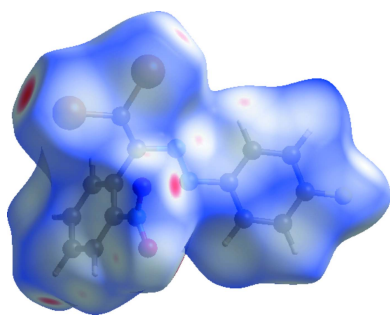
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Physics, Faculty of Sciences, Erciyes University, 38039 Kayseri, Turkey, ^bOrganic Chemistry Department, Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan, ^cPeoples' Friendship University of Russia, 6 Miklukho-Maklaya, Moscow, Russian Federation, ^dN.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Av., Moscow, Russian Federation, and ^eDepartment of Chemistry, M.M.A.M.C (Tribhuvan University) Biratnagar, Nepal. *Correspondence e-mail: bkajaya@yahoo.com

In the title compound, C₁₄H₈Br₂FN₃O₂, the nitro-substituted benzene ring and the 4-fluorophenyl ring form a dihedral angle of 65.73 (7)°. In the crystal, molecules are linked into chains by C—H...O hydrogen bonds running parallel to the *c*-axis direction. The crystal packing is consolidated by C—F... π interactions and π – π stacking interactions, and short Br...O [2.9828 (13) Å] contacts are observed. The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions to the crystal packing are from H...H (17.4%), O...H/H...O (16.3%), Br...H/H...Br (15.5%), Br...C/C...Br (10.1%) and F...H/H...F (8.1%) contacts.

1. Chemical context

Azo dyes are chemical compounds with the general formula $R-N=N-R'$, where R and R' can be either aryl, hetrocycle or alkyl functional groups. They find many applications such as molecular switches, optical data storage, antimicrobial agent, colour-changing materials, non-linear optics, molecular recognition, dye-sensitized solar cells, liquid crystals, catalysis, *etc.* (see, for example, Kopylovich *et al.*, 2012; MacLeod *et al.*, 2012; Viswanathan *et al.*, 2019). Both *E/Z* isomerization and azo-to-hydrazo tautomerization of azo dyes is an important feature in the synthesis and design of new functional materials (Mahmudov *et al.*, 2012, 2020; Mizar *et al.*, 2012). On the other hand, the attachment of non-covalent bond-donor or acceptor centres to the azo dyes can be used as a synthetic strategy for the improvement of the functional properties of this class of organic compounds (Gurbanov *et al.*, 2020*a,b*).



As part of our ongoing work in this area we have attached –F, –Br and –NO₂ functional groups and aryl rings to the –N=N– moiety, leading to the title compound, C₁₄H₈Br₂FN₃O₂, and determined its crystal structure.



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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------|-------|-------------|-------------|---------------|
| $C6-H6\cdots O1^i$ | 0.95 | 2.51 | 3.3244 (18) | 144 |

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

2. Structural commentary

As shown in Fig. 1, the molecular conformation of the title compound is not planar, the nitro-substituted benzene ring and the 4-fluorophenyl ring forming a dihedral angle of $65.73(7)^\circ$. There is a slight twist about the $C1=C2$ double bond with the dihedral angle between $C1/Br1/Br2$ and $C2/C3/N2$ being $3.35(15)^\circ$, perhaps to minimize steric repulsion between $Br2$ and $H8$. Considered together, the $N3/N2/C2/C1/Br1/Br2$ moiety subtends dihedral angles of $70.40(7)$ and $14.14(7)^\circ$ with the $C3-C8$ and $C9-C14$ rings, respectively. In the molecule, the aromatic ring and olefin synthon adopt a *trans*-configuration with respect to the $N=N$ double bond and are almost coplanar with a $C2-N2=N3-C9$ torsion angle of $-178.50(11)^\circ$. All of the other bond lengths and angles in the title compound are similar to those in the related azo compounds reported in the *Database survey*.

3. Supramolecular features

In the crystal, molecules are linked by $C-H\cdots O$ hydrogen bonds into chains propagating parallel to the c axis (Table 1; Fig. 2). The crystal packing is consolidated by weak $C-F\cdots\pi$ [$F1\cdots Cg1(x, 1-y, -\frac{1}{2}+z) = 3.4095(12)$ Å; $C-F\cdots Cg1 = 136.95(9)^\circ$] interactions and weak aromatic $\pi-\pi$ stacking [$Cg2\cdots Cg2(1-x, y, \frac{1}{2}-z) = 3.9694(9)$ Å], where $Cg1$ and $Cg2$ are the centroids of the $C3-C8$ and $C9-C14$ rings, respectively (Fig. 2). In addition, short bromine–oxygen contacts [$Br2\cdots O2(\frac{3}{2}-x, \frac{1}{2}+y, z) = 2.9828(13)$ Å; van der Waals contact distance = 3.37 Å] are observed.

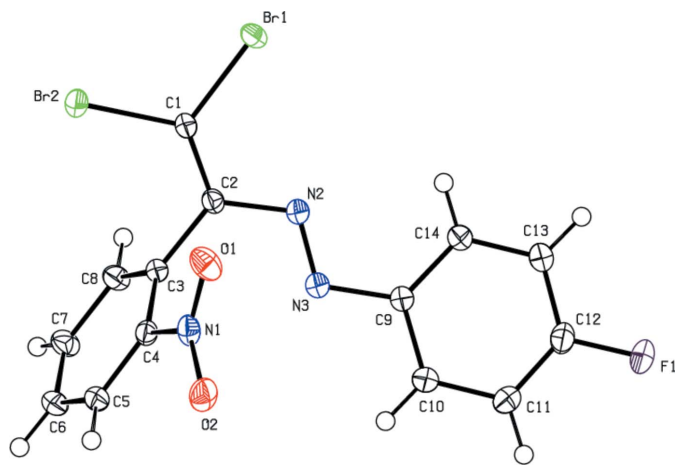


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

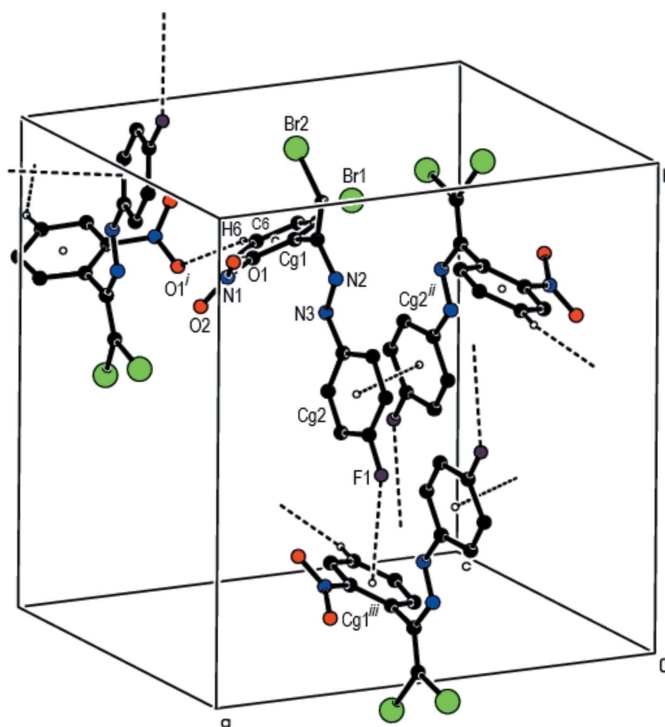


Figure 2
View of the $C-H\cdots O$, $C-F\cdots\pi$ and $\pi-\pi$ stacking interactions in the title compound.

4. Hirshfeld surface analysis

CrystalExplorer17 (Turner *et al.*, 2017) was used to calculate the Hirshfeld surfaces for the title compound and generate the two-dimensional fingerprint plots. On the d_{norm} surface, red, white, and blue regions indicate contacts with distances shorter, longer, and roughly equal to the van der Waals radii for the title compound (Fig. 3, Tables 1 and 2).

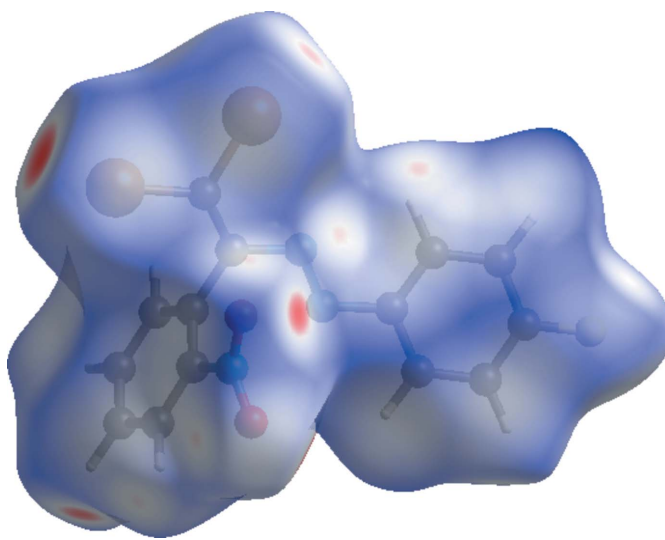


Figure 3
The three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range -0.24 to 1.44 a.u.

Table 2

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

| Contact | Distance | Symmetry operation |
|-----------|----------|--|
| H8···Br1 | 2.99 | $1 - x, y, \frac{1}{2} - z$ |
| O1···H11 | 2.68 | $\frac{3}{2} - x, \frac{1}{2} + y, z$ |
| Br1···Br2 | 3.6164 | $x, 2 - y, -\frac{1}{2} + z$ |
| H7···Br2 | 3.19 | $1 - x, 2 - y, 1 - z$ |
| H13···F1 | 2.82 | $1 - x, 1 - y, -z$ |
| F1···H10 | 2.67 | $x, 1 - y, -\frac{1}{2} + z$ |
| O1···H6 | 2.51 | $\frac{3}{2} - x, \frac{3}{2} - y, -\frac{1}{2} + z$ |
| O2···H8 | 2.77 | $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$ |
| H7···H6 | 2.47 | $1 - x, y, \frac{3}{2} - z$ |

The overall two-dimensional fingerprint plot (Fig. 4a) and those delineated into H···H, O···H/H···O, Br···H/H···Br, Br···C/C···Br and F···H/H···F contacts (McKinnon *et al.*,

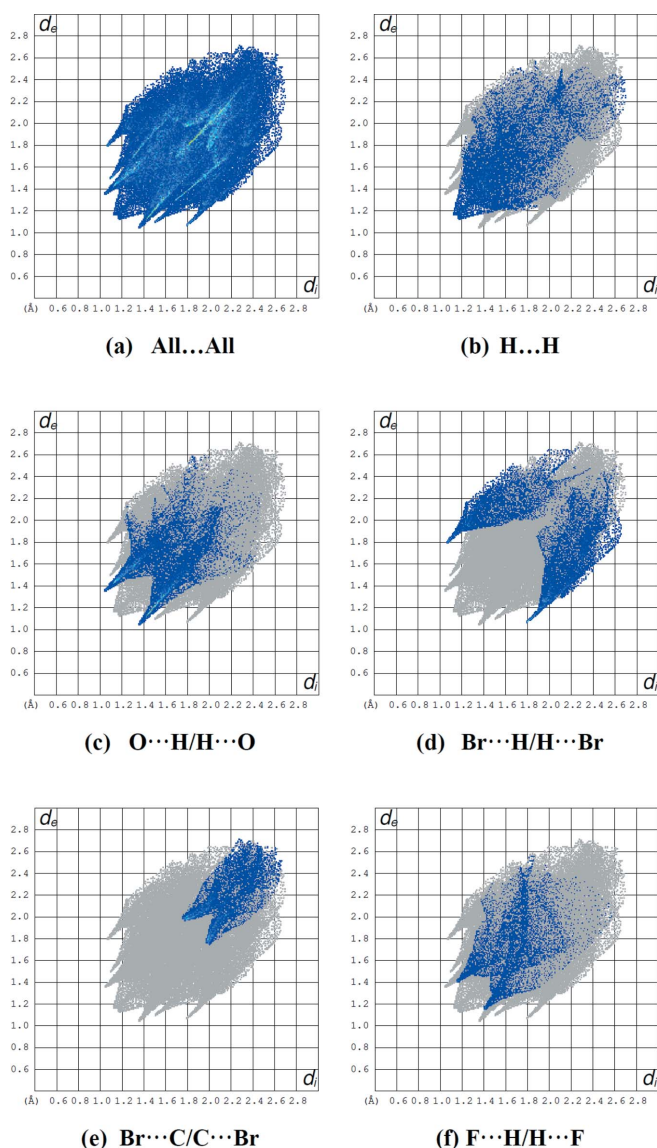


Figure 4

The full two-dimensional fingerprint plot (a) for the title compound and those delineated into (b) H···H (17.4%), (c) O···H/H···O (16.3%), (d) Br···H/H···Br (15.5%), (e) Br···C/C···Br (10.1%) and (f) F···H/H···F (8.1%) interactions.

Table 3

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

| Contact | Percentage contribution |
|---------------|-------------------------|
| H···H | 17.4 |
| O···H/H···O | 16.3 |
| Br···H/H···Br | 15.5 |
| Br···C/C···Br | 10.1 |
| F···H/H···F | 8.1 |
| C···H/H···C | 7.0 |
| N···H/H···N | 5.5 |
| C···C | 4.7 |
| Br···O/O···Br | 4.2 |
| F···C/C···F | 3.5 |
| Br···Br | 3.1 |
| N···C/C···N | 1.4 |
| Br···F/F···Br | 1.1 |
| N···N | 0.9 |
| O···C/C···O | 0.1 |
| F···O/O···F | 0.6 |
| F···N/N···F | 0.5 |

2007) are illustrated in Fig. 4b–f, respectively. The most important interaction is H···H, contributing 17.4% to the overall surface, which is reflected in Fig. 4b as widely scattered points of high density due to the large hydrogen content of the molecule, with the tip at $d_e = d_i = 1.15$ Å. The reciprocal O···H/H···O interactions appear as two symmetrical broad wings with $d_e + d_i \simeq 2.40$ Å and contribute 16.3% to the Hirshfeld surface (Fig. 4c). In the Br···H/H···Br fingerprint plot, there are two symmetrical wings with $d_e + d_i \simeq 2.85$ Å and they contribute 15.5% to the Hirshfeld surface (Fig. 4d). The pair of characteristic wings in the fingerprint plot delineated into Br···C/C···Br contacts (Fig. 8e; 10.1% contribution to the Hirshfeld surface), have the tips at $d_e + d_i \simeq 3.80$ Å, while for F···H/H···F contacts (Fig. 4f; 8.1% contribution to the Hirshfeld surface), they have the tips at $d_e + d_i \simeq 2.60$ Å. The remaining contributions from the other different interatomic contacts to the Hirshfeld surfaces are listed in Table 3. The dominance of H-atom contacts suggest that van der Waals interactions play the major role in establishing the crystal packing for the title compound (Hathwar *et al.*, 2015).

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, update of September 2021; Groom *et al.*, 2016) for the (*E*)-1-(2,2-dichloro-1-phenylethenyl)-2-phenyldiazene unit gave 26 hits. Seven compounds are closely related to the title compound, *viz.* CSD refcode GUPHIL (**I**) (Özkaraca *et al.*, 2020), HONBUK (**II**) (Akkurt *et al.*, 2019), HONBOE (**III**) (Akkurt *et al.*, 2019), HODQAV (**IV**) (Shikhaliyev *et al.*, 2019), XIZREG (**V**) (Atioğlu *et al.*, 2019), LEQXOX (**VI**) (Shikhaliyev *et al.*, 2018) and LEQXIR (**VII**) (Shikhaliyev *et al.*, 2018).

In the crystal of (**I**), molecules are linked into inversion dimers *via* short halogen–halogen contacts [$\text{Cl1}\cdots\text{Cl1} = 3.3763$ (9) Å $\text{Cl6}-\text{Cl1}\cdots\text{Cl1} = 141.47$ (7)°] compared to the van der Waals radius sum of 3.50 Å for two chlorine atoms. No

Table 4
Experimental details.

| | |
|--|---|
| Crystal data | |
| Chemical formula | C ₁₄ H ₈ Br ₂ FN ₃ O ₂ |
| <i>M_r</i> | 429.05 |
| Crystal system, space group | Orthorhombic, <i>Pbcn</i> |
| Temperature (K) | 100 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 14.8700 (4), 15.2915 (4), 13.1030 (4) |
| <i>V</i> (Å ³) | 2979.42 (14) |
| <i>Z</i> | 8 |
| Radiation type | Mo <i>K</i> α |
| <i>μ</i> (mm ⁻¹) | 5.46 |
| Crystal size (mm) | 0.59 × 0.26 × 0.20 |
| Data collection | |
| Diffractometer | Bruker AXS D8 QUEST Photon III detector |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.047, 0.115 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 87568, 5429, 4773 |
| <i>R_{int}</i> | 0.041 |
| (sin θ/λ) _{max} (Å ⁻¹) | 0.758 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.023, 0.057, 1.06 |
| No. of reflections | 5429 |
| No. of parameters | 199 |
| H-atom treatment | H-atom parameters constrained |
| Δρ _{max} , Δρ _{min} (e Å ⁻³) | 0.83, -0.46 |

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

other directional contacts could be identified and the shortest aromatic-ring-centroid separation is greater than 5.25 Å. In the crystals of (**II**) and (**III**), the aromatic rings form dihedral angles of 64.1 (2) and 60.9 (2)°, respectively. Molecules are linked through weak *X*···Cl contacts [*X* = Cl for (**II**) and Br for (**III**)], C–H···Cl and C–Cl···π interactions into sheets lying parallel to the *ab* plane. In the crystal of (**IV**), the planes of the benzene rings make a dihedral angle of 56.13 (13)°. Molecules are stacked in columns along the *a*-axis direction via weak C–H···Cl hydrogen bonds and face-to-face π–π stacking interactions. The crystal packing is further consolidated by short Cl···Cl contacts. In (**V**), the benzene rings form a dihedral angle of 63.29 (8)°. Molecules are linked by C–H···O hydrogen bonds into zigzag chains running along the *c*-axis direction. The crystal packing also features C–Cl···π, C–F···π and N–O···π interactions. In the crystals of (**VI**) and (**VII**), the dihedral angles between the aromatic rings are 60.31 (14) and 56.18 (12)°, respectively. In (**VI**) C–H···N and short Cl···Cl contacts are observed and in (**VII**), C–H···N and C–H···O hydrogen bonds and short Cl···O contacts occur.

6. Synthesis and crystallization

A 20 ml screw-neck vial was charged with DMSO (10 ml), (*E*)-1-(4-fluorophenyl)-2-(2-nitrobenzylidene)hydrazine (1 mmol), tetramethylethylenediamine (TMEDA) (295 mg,

2.5 mmol), CuCl (2 mg, 0.02 mmol) and CBr₄ (4.5 mmol). After 1–3h (until TLC analysis showed complete consumption of corresponding Schiff base) the reaction mixture was poured into a ~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 Na₂SO₄ 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. Light-orange solid (52%); m.p. 377 K. Analysis calculated for C₁₄H₈Br₂FN₃O₂ (*M* = 429.04): C 39.19, H 1.88, N 9.79; found: C 39.14, H 1.87, N 9.73%. ¹H NMR (300MHz, CDCl₃) δ 7.86–7.14 (8H, Ar–H). ¹³C NMR (75MHz, CDCl₃) δ 165.02, 163.23, 163.01, 149.72, 133.01, 132.10, 129.70, 124.98, 124.87, 124.80, 124.29, 116.07, 115.91, 86.88. ESI–MS: *m/z*: 430.02 [*M* + H]⁺.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were positioned geometrically [C–H = 0.95 Å] and refined using a riding model with *U*_{iso}(H) = 1.2*U*_{eq}(C).

Acknowledgements

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

Funding information

This work was performed under the support of the Science Development Foundation under the President of the Republic of Azerbaijan (grant No. EIF-BGM-4- RFTF-1/2017–21/13/4).

References

- Akkurt, M., Shikhaliyev, N. Q., Suleymanova, G. T., Babayeva, G. V., Mammadova, G. Z., Niyazova, A. A., Shikhaliyeva, I. M. & Toze, F. A. A. (2019). *Acta Cryst.* **E75**, 1199–1204.
- Atioğlu, Z., Akkurt, M., Shikhaliyev, N. Q., Suleymanova, G. T., Bagirova, K. N. & Toze, F. A. A. (2019). *Acta Cryst.* **E75**, 237–241.
- Bruker (2018). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Garbanov, A. V., Kuznetsov, M. L., Demukhamedova, S. D., Alieva, I. N., Godjaev, N. M., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2020a). *CrystEngComm*, **22**, 628–633.
- Garbanov, A. V., Kuznetsov, M. L., Mahmudov, K. T., Pombeiro, A. J. L. & Resnati, G. (2020b). *Chem. Eur. J.* **26**, 14833–14837.
- Hathwar, V. R., Sist, M., Jørgensen, M. R. V., Mamakhel, A. H., Wang, X., Hoffmann, C. M., Sugimoto, K., Overgaard, J. & Iversen, B. B. (2015). *IUCrJ*, **2**, 563–574.

- Kopylovich, M. N., MacLeod, T. C. O., Haukka, M., Amanullayeva, G. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *J. Inorg. Biochem.* **115**, 72–77.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- MacLeod, T. C. O., Kopylovich, M. N., Guedes da Silva, M. F. C., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Appl. Catal. Gen.* **439–440**, 15–23.
- Mahmudov, K. T., Guedes da Silva, M. F. C., Glucini, M., Renzi, M., Gabriel, K. C. P., Kopylovich, M. N., Sutradhar, M., Marchetti, F., Pettinari, C., Zamponi, S. & Pombeiro, A. J. L. (2012). *Inorg. Chem. Commun.* **22**, 187–189.
- Mahmudov, K. T., Gurbanov, A. V., Aliyeva, V. A., Resnati, G. & Pombeiro, A. J. L. (2020). *Coord. Chem. Rev.* **418**, 213381.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- Mizar, A., Guedes da Silva, M. F. C., Kopylovich, M. N., Mukherjee, S., Mahmudov, K. T. & Pombeiro, A. J. L. (2012). *Eur. J. Inorg. Chem.* pp. 2305–2313.
- Özkaraca, K., Akkurt, M., Shikhaliyev, N. Q., Askerova, U. F., Suleymanova, G. T., Mammadova, G. Z. & Shadrack, D. M. (2020). *Acta Cryst. E* **76**, 1251–1254.
- Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.
- Shikhaliyev, N. Q., Ahmadova, N. E., Gurbanov, A. V., Maharramov, A. M., Mammadova, G. Z., Nenajdenko, V. G., Zubkov, F. I., Mahmudov, K. T. & Pombeiro, A. J. L. (2018). *Dyes Pigments*, **150**, 377–381.
- Shikhaliyev, N. Q., Kuznetsov, M. L., Maharramov, A. M., Gurbanov, A. V., Ahmadova, N. E., Nenajdenko, V. G., Mahmudov, K. T. & Pombeiro, A. J. L. (2019). *CrystEngComm*, **21**, 5032–5038.
- Spek, A. L. (2020). *Acta Cryst. E* **76**, 1–11.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. The University of Western Australia.
- Viswanathan, A., Kute, D., Musa, A., Mani, S. K., Sipilä, V., Emmert-Streib, F., Zubkov, F. I., Gurbanov, A. V., Yli-Harja, O. & Kandhavelu, M. (2019). *Eur. J. Med. Chem.* **166**, 291–303.

supporting information

Acta Cryst. (2022). E78, 404-408 [https://doi.org/10.1107/S205698902200278X]

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

Sevim Türktekin Çelikesir, Mehmet Akkurt, Namiq Q. Shikhaliyev, Naila A. Mammadova, Gulnar T. Suleymanova, Victor N. Khrustalev and Ajaya Bhattarai

Computing details

Data collection: *APEX3* (Bruker, 2018); cell refinement: *SAINTE* (Bruker, 2018); data reduction: *SAINTE* (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*)-1-[2,2-Dibromo-1-(2-nitrophenyl)ethenyl]-2-(4-fluorophenyl)diazene

Crystal data

$C_{14}H_8Br_2FN_3O_2$

$M_r = 429.05$

Orthorhombic, *Pbcn*

$a = 14.8700$ (4) Å

$b = 15.2915$ (4) Å

$c = 13.1030$ (4) Å

$V = 2979.42$ (14) Å³

$Z = 8$

$F(000) = 1664$

$D_x = 1.913$ Mg m⁻³

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

Cell parameters from 9970 reflections

$\theta = 2.5$ – 34.3°

$\mu = 5.46$ mm⁻¹

$T = 100$ K

Block, light orange

$0.59 \times 0.26 \times 0.20$ mm

Data collection

Bruker AXS D8 QUEST Photon III detector
diffractometer

Radiation source: fine-focus sealed X-Ray tube

Graphite monochromator

Detector resolution: 7.31 pixels mm⁻¹

φ and ω shutterless scans

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

$T_{\min} = 0.047$, $T_{\max} = 0.115$

87568 measured reflections

5429 independent reflections

4773 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 32.6^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -22 \rightarrow 22$

$k = -23 \rightarrow 23$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.057$

$S = 1.06$

5429 reflections

199 parameters

0 restraints

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

$$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.6564P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$

$$\Delta\rho_{\max} = 0.83 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$$

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.

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Br1 | 0.62265 (2) | 0.95963 (2) | 0.16792 (2) | 0.02193 (4) |
| Br2 | 0.64744 (2) | 1.02154 (2) | 0.39424 (2) | 0.02154 (4) |
| F1 | 0.61074 (8) | 0.42468 (7) | 0.03550 (8) | 0.0350 (2) |
| O1 | 0.79994 (8) | 0.81157 (8) | 0.37024 (8) | 0.0279 (2) |
| O2 | 0.82768 (8) | 0.70323 (8) | 0.47212 (9) | 0.0279 (2) |
| N1 | 0.78022 (8) | 0.76388 (8) | 0.44249 (9) | 0.0204 (2) |
| N2 | 0.61421 (8) | 0.77830 (8) | 0.26409 (9) | 0.0173 (2) |
| N3 | 0.61871 (8) | 0.70235 (8) | 0.30197 (9) | 0.0180 (2) |
| C1 | 0.62788 (9) | 0.92776 (9) | 0.30578 (10) | 0.0172 (2) |
| C2 | 0.62325 (9) | 0.84437 (9) | 0.33887 (9) | 0.0163 (2) |
| C3 | 0.62473 (9) | 0.82188 (9) | 0.44946 (10) | 0.0160 (2) |
| C4 | 0.69718 (9) | 0.78201 (9) | 0.49868 (10) | 0.0167 (2) |
| C5 | 0.69526 (10) | 0.75800 (9) | 0.60064 (10) | 0.0198 (2) |
| H5 | 0.745761 | 0.730610 | 0.631466 | 0.024* |
| C6 | 0.61793 (10) | 0.77479 (10) | 0.65687 (10) | 0.0216 (3) |
| H6 | 0.615605 | 0.760257 | 0.727309 | 0.026* |
| C7 | 0.54428 (10) | 0.81279 (10) | 0.60985 (10) | 0.0221 (3) |
| H7 | 0.491119 | 0.823434 | 0.648092 | 0.026* |
| C8 | 0.54741 (10) | 0.83559 (9) | 0.50689 (10) | 0.0195 (2) |
| H8 | 0.495992 | 0.860845 | 0.475544 | 0.023* |
| C9 | 0.61222 (9) | 0.63404 (9) | 0.22921 (10) | 0.0173 (2) |
| C10 | 0.62860 (10) | 0.55039 (9) | 0.26748 (11) | 0.0214 (3) |
| H10 | 0.640277 | 0.542361 | 0.338142 | 0.026* |
| C11 | 0.62783 (11) | 0.47892 (10) | 0.20219 (13) | 0.0253 (3) |
| H11 | 0.639299 | 0.421601 | 0.226931 | 0.030* |
| C12 | 0.60996 (11) | 0.49353 (11) | 0.10055 (12) | 0.0245 (3) |
| C13 | 0.59060 (10) | 0.57525 (10) | 0.06081 (11) | 0.0224 (3) |
| H13 | 0.577105 | 0.582364 | -0.009565 | 0.027* |
| C14 | 0.59139 (10) | 0.64622 (9) | 0.12606 (10) | 0.0194 (2) |
| H14 | 0.577851 | 0.703011 | 0.101002 | 0.023* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.02940 (8) | 0.02164 (7) | 0.01475 (6) | -0.00253 (5) | -0.00260 (5) | 0.00271 (5) |
| Br2 | 0.02785 (8) | 0.01832 (7) | 0.01843 (6) | -0.00056 (5) | 0.00111 (5) | -0.00383 (5) |
| F1 | 0.0542 (7) | 0.0220 (5) | 0.0287 (5) | 0.0035 (5) | -0.0047 (4) | -0.0101 (4) |
| O1 | 0.0232 (5) | 0.0403 (6) | 0.0201 (5) | 0.0021 (5) | 0.0046 (4) | 0.0009 (4) |
| O2 | 0.0267 (5) | 0.0279 (6) | 0.0292 (6) | 0.0120 (5) | -0.0039 (4) | -0.0073 (4) |
| N1 | 0.0184 (5) | 0.0245 (6) | 0.0183 (5) | 0.0033 (5) | -0.0014 (4) | -0.0066 (4) |
| N2 | 0.0197 (5) | 0.0170 (5) | 0.0152 (5) | 0.0005 (4) | 0.0008 (4) | -0.0012 (4) |
| N3 | 0.0200 (5) | 0.0178 (5) | 0.0161 (5) | 0.0002 (4) | 0.0002 (4) | -0.0008 (4) |
| C1 | 0.0205 (6) | 0.0179 (6) | 0.0134 (5) | 0.0009 (5) | 0.0000 (4) | -0.0017 (4) |
| C2 | 0.0170 (5) | 0.0182 (6) | 0.0136 (5) | 0.0015 (5) | 0.0003 (4) | -0.0012 (4) |
| C3 | 0.0185 (6) | 0.0154 (5) | 0.0140 (5) | 0.0012 (5) | -0.0003 (4) | -0.0006 (4) |
| C4 | 0.0181 (6) | 0.0160 (5) | 0.0161 (5) | 0.0014 (5) | -0.0004 (4) | -0.0026 (4) |
| C5 | 0.0236 (6) | 0.0192 (6) | 0.0166 (5) | 0.0031 (5) | -0.0031 (5) | -0.0001 (4) |
| C6 | 0.0278 (7) | 0.0218 (6) | 0.0151 (5) | 0.0021 (5) | 0.0006 (5) | 0.0022 (5) |
| C7 | 0.0235 (7) | 0.0262 (7) | 0.0165 (6) | 0.0037 (5) | 0.0046 (5) | 0.0027 (5) |
| C8 | 0.0192 (6) | 0.0229 (6) | 0.0162 (5) | 0.0036 (5) | 0.0011 (4) | 0.0022 (5) |
| C9 | 0.0183 (6) | 0.0173 (6) | 0.0162 (5) | 0.0002 (5) | 0.0001 (4) | -0.0007 (4) |
| C10 | 0.0258 (7) | 0.0192 (6) | 0.0191 (6) | 0.0013 (5) | -0.0022 (5) | 0.0009 (5) |
| C11 | 0.0321 (8) | 0.0180 (6) | 0.0259 (7) | 0.0029 (6) | -0.0028 (6) | -0.0009 (5) |
| C12 | 0.0289 (7) | 0.0213 (6) | 0.0232 (7) | 0.0004 (6) | -0.0013 (5) | -0.0063 (5) |
| C13 | 0.0273 (7) | 0.0225 (7) | 0.0175 (6) | -0.0003 (6) | -0.0012 (5) | -0.0027 (5) |
| C14 | 0.0224 (6) | 0.0189 (6) | 0.0168 (5) | -0.0006 (5) | 0.0001 (5) | 0.0001 (4) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-------------|----------|-------------|
| Br1—C1 | 1.8725 (13) | C6—C7 | 1.384 (2) |
| Br2—C1 | 1.8667 (13) | C6—H6 | 0.9500 |
| F1—C12 | 1.3546 (17) | C7—C8 | 1.3942 (18) |
| O1—N1 | 1.2304 (17) | C7—H7 | 0.9500 |
| O2—N1 | 1.2284 (16) | C8—H8 | 0.9500 |
| N1—C4 | 1.4641 (18) | C9—C10 | 1.3953 (19) |
| N2—N3 | 1.2647 (16) | C9—C14 | 1.3992 (19) |
| N2—C2 | 1.4138 (17) | C10—C11 | 1.388 (2) |
| N3—C9 | 1.4175 (17) | C10—H10 | 0.9500 |
| C1—C2 | 1.3486 (19) | C11—C12 | 1.376 (2) |
| C2—C3 | 1.4895 (18) | C11—H11 | 0.9500 |
| C3—C8 | 1.3900 (19) | C12—C13 | 1.384 (2) |
| C3—C4 | 1.3958 (18) | C13—C14 | 1.382 (2) |
| C4—C5 | 1.3859 (18) | C13—H13 | 0.9500 |
| C5—C6 | 1.390 (2) | C14—H14 | 0.9500 |
| C5—H5 | 0.9500 | | |
| O2—N1—O1 | 123.62 (13) | C6—C7—H7 | 119.7 |
| O2—N1—C4 | 117.94 (13) | C8—C7—H7 | 119.7 |
| O1—N1—C4 | 118.41 (12) | C3—C8—C7 | 120.92 (13) |

| | | | |
|--------------|--------------|-----------------|--------------|
| N3—N2—C2 | 112.28 (11) | C3—C8—H8 | 119.5 |
| N2—N3—C9 | 114.15 (11) | C7—C8—H8 | 119.5 |
| C2—C1—Br2 | 122.32 (10) | C10—C9—C14 | 120.52 (13) |
| C2—C1—Br1 | 123.65 (10) | C10—C9—N3 | 114.96 (12) |
| Br2—C1—Br1 | 113.92 (7) | C14—C9—N3 | 124.52 (12) |
| C1—C2—N2 | 117.24 (12) | C11—C10—C9 | 119.93 (14) |
| C1—C2—C3 | 122.03 (12) | C11—C10—H10 | 120.0 |
| N2—C2—C3 | 120.71 (12) | C9—C10—H10 | 120.0 |
| C8—C3—C4 | 117.01 (12) | C12—C11—C10 | 118.05 (14) |
| C8—C3—C2 | 118.66 (12) | C12—C11—H11 | 121.0 |
| C4—C3—C2 | 124.19 (12) | C10—C11—H11 | 121.0 |
| C5—C4—C3 | 123.04 (13) | F1—C12—C11 | 118.75 (14) |
| C5—C4—N1 | 116.88 (12) | F1—C12—C13 | 117.83 (13) |
| C3—C4—N1 | 120.08 (12) | C11—C12—C13 | 123.42 (14) |
| C4—C5—C6 | 118.63 (13) | C14—C13—C12 | 118.34 (13) |
| C4—C5—H5 | 120.7 | C14—C13—H13 | 120.8 |
| C6—C5—H5 | 120.7 | C12—C13—H13 | 120.8 |
| C7—C6—C5 | 119.75 (12) | C13—C14—C9 | 119.68 (13) |
| C7—C6—H6 | 120.1 | C13—C14—H14 | 120.2 |
| C5—C6—H6 | 120.1 | C9—C14—H14 | 120.2 |
| C6—C7—C8 | 120.61 (13) | | |
| | | | |
| C2—N2—N3—C9 | -178.50 (11) | C3—C4—C5—C6 | -0.4 (2) |
| Br2—C1—C2—N2 | -175.87 (9) | N1—C4—C5—C6 | 179.45 (13) |
| Br1—C1—C2—N2 | 0.19 (18) | C4—C5—C6—C7 | 1.6 (2) |
| Br2—C1—C2—C3 | 5.92 (19) | C5—C6—C7—C8 | -1.0 (2) |
| Br1—C1—C2—C3 | -178.02 (10) | C4—C3—C8—C7 | 2.0 (2) |
| N3—N2—C2—C1 | 173.96 (13) | C2—C3—C8—C7 | 177.74 (13) |
| N3—N2—C2—C3 | -7.80 (18) | C6—C7—C8—C3 | -0.9 (2) |
| C1—C2—C3—C8 | 75.95 (18) | N2—N3—C9—C10 | 172.10 (13) |
| N2—C2—C3—C8 | -102.20 (16) | N2—N3—C9—C14 | -7.8 (2) |
| C1—C2—C3—C4 | -108.63 (17) | C14—C9—C10—C11 | 2.6 (2) |
| N2—C2—C3—C4 | 73.22 (18) | N3—C9—C10—C11 | -177.28 (14) |
| C8—C3—C4—C5 | -1.4 (2) | C9—C10—C11—C12 | -0.5 (2) |
| C2—C3—C4—C5 | -176.84 (13) | C10—C11—C12—F1 | 178.69 (15) |
| C8—C3—C4—N1 | 178.78 (12) | C10—C11—C12—C13 | -1.7 (3) |
| C2—C3—C4—N1 | 3.3 (2) | F1—C12—C13—C14 | -178.71 (14) |
| O2—N1—C4—C5 | 26.58 (18) | C11—C12—C13—C14 | 1.6 (2) |
| O1—N1—C4—C5 | -151.37 (13) | C12—C13—C14—C9 | 0.5 (2) |
| O2—N1—C4—C3 | -153.54 (13) | C10—C9—C14—C13 | -2.6 (2) |
| O1—N1—C4—C3 | 28.51 (19) | N3—C9—C14—C13 | 177.24 (13) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C6—H6 \cdots O1 ⁱ | 0.95 | 2.51 | 3.3244 (18) | 144 |

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