UNEC Journal of Engineering and Applied Sciences
Vol. 3, No.1, 2023, pp. 33-39

SECTION: CHEMISTRY

Crystal structure and Hirshfeld surface analysis of (E)-1-(4-chlorophenyl)-2-(2,2-dibromo-1-(3-nitrophenyl)vinyl)diazene

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Abstract

The molecule of the title compound, $C_{14}H_8Br_2ClN_3O_2$, 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 17.00 (13) and 60.91 (13)^0 for chlorine- and nitro-substituted rings, respectively. In the crystal, face-to-face π-π stacking interactions connect molecules in zig-zag chains along the a-axis. With halogen···halogen, halogen···hydrogen, Br···H, O···H, N···H and van der Waals interactions between these chains, molecular packing becomes stable. The most substantial contributions to crystal packing, according to a Hirshfeld surface analysis, are from Br···H/H···Br (19.6%), H···H (12.2%), C···H/H···C (11.9%) and O···H/H···O (11.0%) contacts.

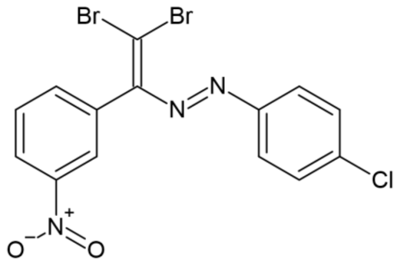
***Keywords**:* crystal structure, face-to-face π-π stacking interactions, van der Waals interactions, Hirshfeld surface analysis.

PACS numbers: 61.66.Hq, 61.66.-f, 61.90.+d

Received: 13 march 2023 *Accepted: 05 april 2023* *Published: 29 may 2023*

1. Introduction

Azo dyes are a large class of synthetic organic dyes that contain nitrogen as the azo group R-N=N-R' (R and R' can be either alkyl, aryl or hetrocycle functional groups) as part of their molecular structures [1,2]. Depending on the attached functional groups the azo dyes have attracted much attention because of their high synthetic potential for organic and inorganic chemistries as well as diverse useful properties. For example, azo compounds can find applications in self-assembled layers, spectrophotometric reagents for determination of metal ions, design of functional materials attributed to smart hydrogen bonding, liquid crystals, photo-triggered structural switching, ionophors, optical recording media, indicators, semiconductors, catalysts, photoluminescent materials, spin-coating films, antimicrobial agent, etc. [3-6]. Both E/Z isomerization and azo-to-hydrazo tautomerisation properties of azo dyes is an important phenomena in synthesis and design of new functional materials [7,8]. Moreover, a decoration of azocompounds with the noncovalent bond donor or acceptor centres can be used as a syntheric strategy in the improvement of functional properties of this class of organic compounds [9-12]. Thus, we have attached –Cl and –NO_2 and aryl rings to the –N=N– moiety leading to a new azocompound, (*E*)-1-(4-chlorophenyl)-2-(2,2-dibromo-1-(3-nitrophenyl)vinyl) diazene, which can be provide intermolecular halogen and hydrogen bonds as well as π-interactions.



2. Experiments

This dye was synthesized according to the reported method [13-20]. A 20mL screw neck vial was charged with DMSO (10mL), (*E*)-1-(4-chlorophenyl)-2-(3-nitrobenzylidene)hydrazine (1mmol), tetramethylethylenediamine (TMEDA) (295mg, 2.5 mmol), CuCl (2mg, 0.02 mmol) and CBr$_4$ (4.5mmol). After 1-3h (until TLC analysis showed complete consumption of corresponding Schiff base) reaction mixture was poured into ~0.01 M solution of HCl (100mL, ~pH = 2-3), and extracted with dichloromethane (3x20 mL). The combined organic phase was washed with water (3x50 mL), brine (30mL), dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo of the 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. Yellow solid (57 %); mp 381K. Anal. Calcd for C$_{14}$H$_8$Br$_2$ClN$_3$O$_2$ (M = 445.50): C 37.75, H 1.81, N 9.43; found: C 34.27, H 1.70, N 8.56 %. ^{1}H NMR (300MHz, CDCl$_3$) δ 8.30 – 7.43 (8H, Ar–H). ^{13}C NMR (75MHz, CDCl$_3$) δ 146.32, 143.54, 133.68, 131.42, 131.26, 124.95, 124.70, 120.45, 120.08, 119.14, 118.61, 107.86. ESI-MS: m/z: 446.6 [M+H]$^+$.

3. Result and discussion

The molecule of the title compound (Figure 1) consists of three almost planar groups: the central dibromoethenyldiazene fragment [largest deviation from the l.s. plane is 0.177 (1) Å for Br1] and two attached aromatic rings. The mean planes of these rings form dihedral angles with the plane of the central fragment of 17.00 (13) and 60.91 (13)° for the chlorine- and nitro-substituted rings, respectively. The nitro group is twisted by 12.3 (2)° with respect to the C3–C8 aromatic ring. The C2—N1 bond distance of 1.420 (4) Å indicates π-conjugation between ethene and diazo groups. All other bond lengths and angles in the title compound are similar to those reported for the related azo compounds discussed in the Database survey section.

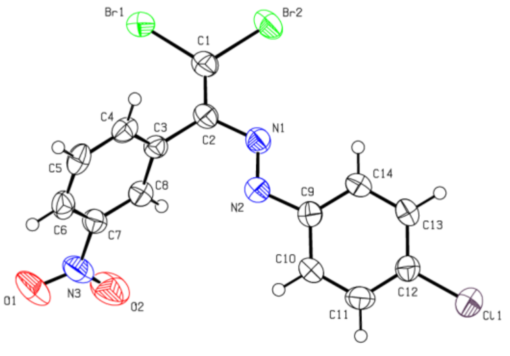


Figure 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

In the crystal, face-to-face - stacking interactions [Cg1⋯Cg1i = 3.824 (2) Å and Cg1⋯Cg1ii = 3.824 (2) Å; symmetry codes (i) -1/2 + x, y, 3/2-z; (ii) 1/2 + x, y, 3/2 - z; Cg1 is a centroid of the (C3–C8) nitrophenyl ring] join molecules in zig-zag chains along the a-axis (Figure 2, 3 and 4). Molecular packing becomes stable with halogen⋯halogen, halogen⋯hydrogen, Br⋯H, O⋯H, N⋯H and van der Waals interactions between these chains (Table 1).

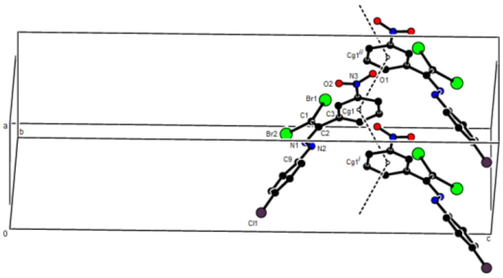


Figure 2. View in the unit cell of the title compound showing the face-to-face π-π stacking interactions. Symmetry codes (*i*) -1/2 + x, y, 3/2-z; (*ii*) 1/2 + x, y, 3/2 - z.

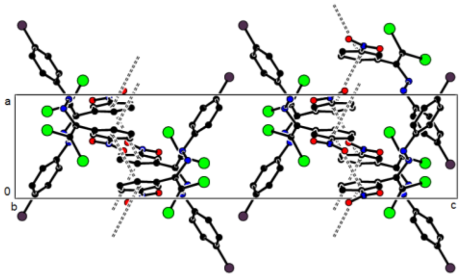


Figure 3. View down the b-axis of the title compound showing the face-to-face π-π stacking interactions.

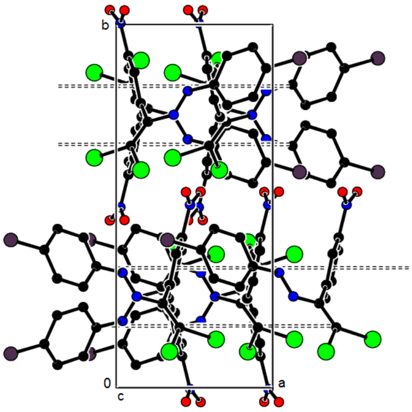


Figure 4. View down the c-axis of the title compound showing the face-to-face π-π stacking interactions.

Crystal Explorer 17.5 [21] was used to perform a Hirshfeld surface analysis and generate the corresponding two-dimensional fingerprint plots, with a standard resolution of the three-dimensional dnorm surfaces plotted over a fixed color scale of -0.0877 (red) to 1.1841 (blue) (Figure 5). The red areas on the surface reflect short contacts and negative d_{norm} values, which correspond to halogen⋯halogen, halogen⋯hydrogen, Br⋯H, O⋯H and N⋯H contacts explained above (Table 1).

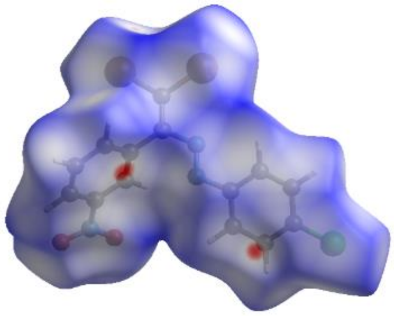
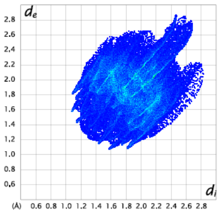
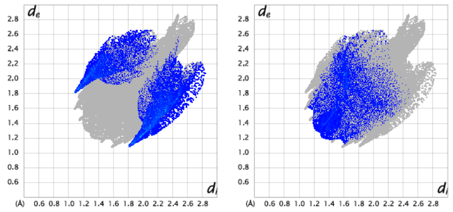


Figure 5. View of the three-dimensional Hirshfeld surface of the title compound plotted over d_{norm} in the range -0.0877 to 1.1841 a.u.

The overall two-dimensional fingerprint plot for the title compound and those delineated into Br···H/H···Br (19.6%), H···H (12.2%), C···H/H···C (11.9%) and O···H/H···O (11.0%) contacts are shown in Fig.6, while numerical details for short intermolecular contacts are given in Table 2. Cl···H/H···Cl (7.8%), N···H/H···N (5.5%), C···C (5.5%), Br···O/O···Br (5.4%), Br···Cl/Cl···Br (5.3%), Br···C/C···Br (4.1%), Cl···C/C···Cl (3.3%), O···C/C···O (2.5%), N···O/O···N (1.7%), Cl···N/N···Cl (1.5%), O···O (1.2%), Br···N/N···Br (0.8%), N···C/C···N (0.5%) and Cl···Cl (0.3%) contacts have little directional influence on the molecular packing.

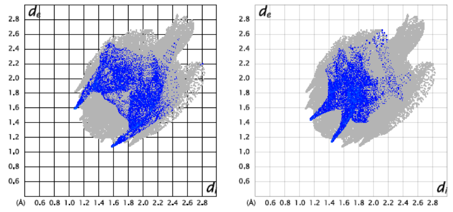


(a) All…All



(b) Br···H/H··· Br

(c) H…H



(d) C···H/H···C

(e) O···H/H···O

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

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were geometrically positioned and constrained to ride on their parent atoms (C—H = 0.93 Å) with $U_{iso}(H) = 1.2U_{eq}(C)$.

Contact	Distance	Summetry operation
H8A···C11	2.77	1+x,y,z
H4A···O1	2.70	2-x,-1/2+y,3/2-z
H5A···N2	2.88	1/2+x,y,3/2-z
Br1···O2	3.25	5/2-x,-1/2+y,z
Br1···H10A	3.02	3/2-x,-1/2+y,z
Br2···Cl1	3.65	1/2-x,-1/2+y,z
Cl1···H14A	2.99	-1/2+x,1/2-y,1-z
C11···Cl1	3.61	-x,1-y,1-z

Table 1. Summary of short interatomic contacts (Å) in the title compound

Chemical formula	$C_{14}H_8Br_2ClN_3O_2$
M_r	445.50
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, b, c (Å)	6.7965 (8), 15.7932 (16), 28.994 (3)
V (Å^3)	3112.2 (6)
Z	8
Radiation type (mm)	Mo
μ (mm^{-1})	5.39
Crystal size	0.23×0.16×0.13
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS* (Bruker, 2007)
T_{min}, T_{max}	0.369, 0.496
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	31512, 2651, 2053
R_{int}	0.077
(sin θ/λ)$_{max}$ (Å^{-1})	0.589
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.066, 1.01
No. of reflections	2651
No. of parameters	199
H – atom treatement	H – atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, –0.38

Computer programs: APEX-II [21], SAINT [21], SHELXT [23], SHELXL2014 [24], WinGX [25] and PLATON [26].

Table 2. Experimental details

A search of the Cambridge Structural Database [27] for similar structures with the (E)-1-(2,2-dibromo)-2-(4-bromophenyl)diazene unit showed that the eleven closest are those of CSD refcodes TAZDIL (I) [28], HEHKEO (II) [29], ECUDAL (III) [30], PAXDOL (IV) [31], GUPHIL (V) [1, HONBUK (VI) [13], HONBOE (VII) [13], HODQAV (VIII) [20], XIZREG (IX) [14], LEQXOX (X) [19] and LEQXIR (XI) [19].

The molecules in (I) are joined into layers parallel to (011) by C—H···O and C—H···F hydrogen bonds. C—Br···π and C—F···π contacts, as well as π–π stacking interactions, strengthen the crystal packing.

In the crystal of the form-1 polymorph of the compound (II), C—H···Br interactions connect the molecules, resulting in zigzag C(8) chains along the [100] direction. These chains are connected by C—Br···π interactions into layers parallel to (001). van der Waals interactions between the layers

A new polymorph of the compound (III), (form-2) was obtained in the same manner as the previously reported form-1 (II) [29]. The structure of the new polymorph is stabilized by a C—H···O hydrogen bond that links molecules into chains. These chains are linked by face-to-face π–π stacking interactions, resulting in a layered structure. Short inter-molecular Br···O contacts and van der Waals interactions between the layers aid in the cohesion of the crystal packing.

The molecules in the crystal of (IV) are connected into chains running parallel to [001] by C—H···O hydrogen bonds. C—F···π contacts and π–π stacking interactions help to consolidate the crystal packing, and short Br···O [2.9828 (13) Å] distances are also observed. In the crystal of (V), the molecules are linked into inversion dimers via short halogen–halogen contacts [Cl1···Cl1 = 3.3763 (9) Å, C16—Cl1···Cl1 = 141.47 (7)° compared to the van der Waals radii 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 (VI) and (VII), the molecules are linked through weak X···Cl contacts [X= Cl for (VI) and Br for (VII)], C—H···Cl and C—Cl···π interactions into sheets lying parallel to (001).

In the crystal of (VIII), the molecules are stacked in columns along [100] 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 (IX), molecules are linked by C—H···O hydrogen bonds into zigzag chains running parallel to [001]. The crystal packing also features C—Cl···π, C—F···π and N—O···π interactions.

In (X), C—H···N and short Cl···Cl contacts are observed, and in (XI), C—H···N and C—H···O hydrogen bonds and short Cl···O contacts occur.

4. Conclusion

Our molecule is linked in zig-zag chains along the a-axis by face-to-face π-π stacking interactions. Molecular packing becomes stable with halogen···halogen, halogen···hydrogen, Br···H, O···H, N···H and van der Waals interactions between these chains.

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