

# Crystal structure and Hirshfeld surface analysis of (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)-hydrazine

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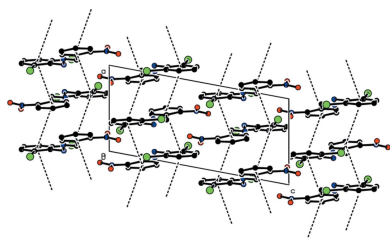
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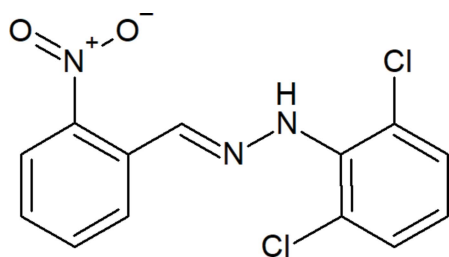
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In the title compound,  $C_{13}H_9Cl_2N_3O_2$ , the 2,6-dichlorophenyl ring and the nitro-substituted benzene ring form a dihedral angle of  $21.16(14)^\circ$ . In the crystal, face-to-face  $\pi$ - $\pi$  stacking interactions occur along the *a*-axis direction between the centroids of the 2,6-dichlorophenyl ring and the nitro-substituted benzene ring. Furthermore, these molecules show intramolecular N-H $\cdots$ Cl and C-H $\cdots$ O contacts and are linked by intermolecular N-H $\cdots$ O and C-H $\cdots$ Cl hydrogen bonds, forming pairs of hydrogen-bonded molecular layers parallel to (20 $\bar{2}$ ). The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions to the crystal packing are from H $\cdots$ H (23.0%), O $\cdots$ H/H $\cdots$ O (20.1%), Cl $\cdots$ H/H $\cdots$ Cl (19.0%), C $\cdots$ C (11.2%) and H $\cdots$ C/C $\cdots$ H (8.0%) interactions.

## 1. Chemical context

Arylhydrazones and their complexes have attracted much attention because of their high synthetic potential for organic and inorganic chemistry and diverse useful properties (Maharramov *et al.*, 2009, 2010, 2018; Mahmudov *et al.*, 2010, 2011, 2014*a*). The analytical and catalytic properties of this class of compounds are strongly dependent on the attached groups to the hydrazone moiety (Mahmudov *et al.*, 2013; Shikhaliyev *et al.*, 2018, 2019). On the other hand, intermolecular interactions organize the molecular architectures, which play a critical role in synthesis, catalysis, micellization, *etc.* (Akbari Afkhami *et al.*, 2017; Gurbanov *et al.*, 2017, 2018; Kopylovich *et al.*, 2011*a,b*; Ma *et al.*, 2017*a,b*; Mahmoudi *et al.*, 2016, 2017*a,b,c*, 2018*a,b*). New types of non-covalent bonds such as halogen, chalcogen, pnictogen and tetrel bonds or their cooperation with hydrogen bonds are able to contribute to the synthesis and catalysis, giving materials with improved properties (Mahmudov *et al.*, 2013, 2014*b*, 2015, 2017*a,b*, 2019; Mizar *et al.*, 2012; Shikhaliyev *et al.*, 2013, 2014). For that, the main skeleton of the hydrazone ligand should be decorated by non-covalent bond donor centre(s). In a continuation of our work in this regard, we have functionalized a new azo dye, (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine, which provides intermolecular non-covalent interactions.



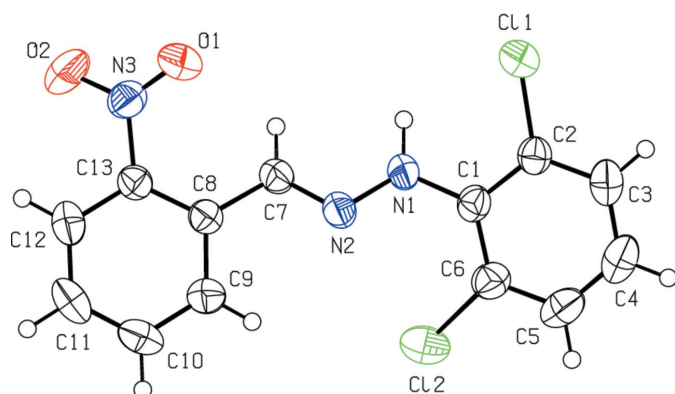


## 2. Structural commentary

The title molecule (Fig. 1) has an *E* configuration about the C=N bond. The 2,6-dichlorophenyl ring and the nitro-substituted benzene ring of the title compound are inclined at 21.16 (14)°, while the nitro group is skewed out of the attached benzene ring plane by 27.06 (18)°. The Cl1–C2–C1–N1, Cl2–C6–C1–N1, C2–C1–N1–N2, C1–N1–N2–C7, N1–N2–C7–C8, N2–C7–C8–C13, C7–C8–C13–N3, C8–C13–N3–O1 and C8–C13–N3–O2 torsion angles are 0.1 (3), 4.7 (4), –145.8 (2), 176.7 (2), 175.4 (2), 164.3 (3), –7.7 (4), –26.9 (4) and 155.7 (3)°, respectively. Two intramolecular N–H···Cl and C–H···O contacts are present (Table 1).

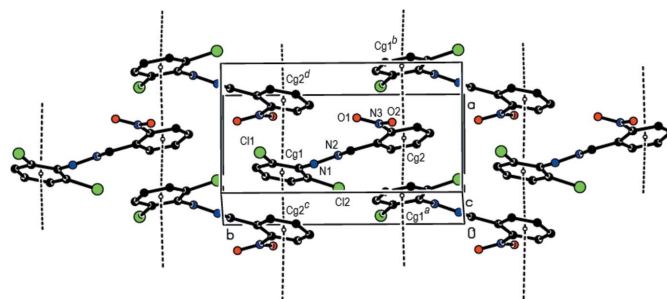
## 3. Supramolecular features and Hirshfeld surface analysis

In the crystal, face-to-face  $\pi$ – $\pi$  stacking interactions [ $Cg1 \cdots Cg2(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z) = 3.7605$  (17) Å with slippage of 1.352 Å,  $Cg1 \cdots Cg2(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z) = 3.8010$  (17) Å with slippage of 1.457 Å, where  $Cg1$  and  $Cg2$  are the centroids of the C1–C6 and C8–C13 rings, respectively] occur between the centroids of the 2,6-dichlorophenyl ring and the nitro-substituted benzene ring of the title molecule along the *a*-axis direction (Figs. 2 and 3). Furthermore, these molecules are linked by intermolecular N–H···O and C–H···Cl hydrogen bonds, forming pairs of hydrogen-bonded molecular layers parallel to (20 $\bar{2}$ ) (Tables 1 and 2; Figs. 4 and 5). There is also a C–Cl···Cg interaction [ $Cl1 \cdots Cg2(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z) =$



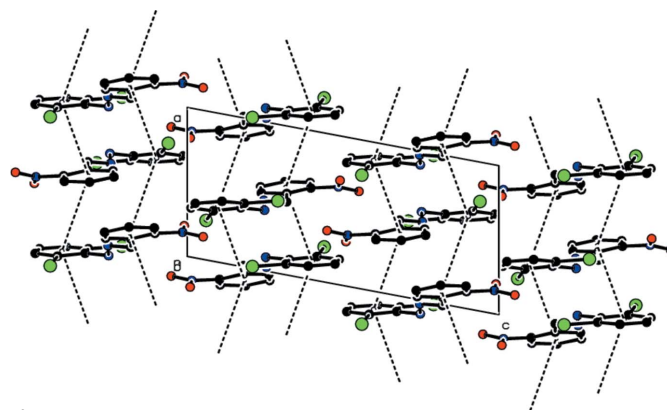
**Figure 1**

The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.



**Figure 2**

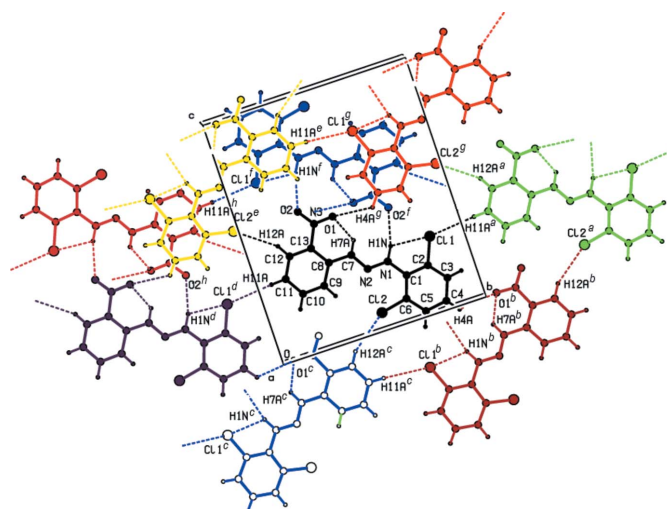
A view of  $\pi$ – $\pi$  stacking interactions in the crystal packing of the title compound.  $Cg1$  and  $Cg2$  are the centroids of the C1–C6 and C8–C13 benzene rings, respectively. [Symmetry codes: (a)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (b)  $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$ ; (c)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (d)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ].



**Figure 3**

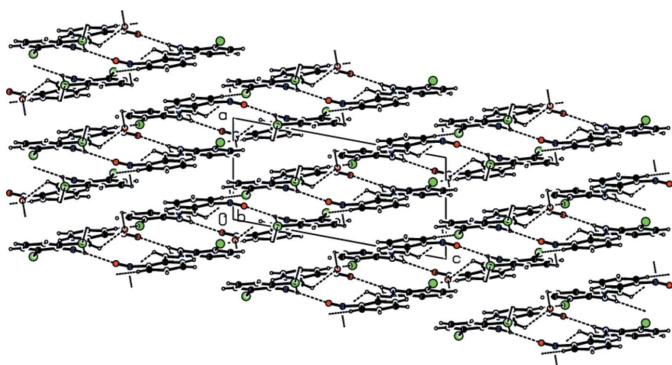
A partial view of  $\pi$ – $\pi$  stacking interactions in the crystal packing of the title compound viewed along the *b* axis.

3.9026 (14) Å;  $C2 - Cl1 \cdots Cg2 = 64.12$  (10)°]. As a result of the large Cl  $\cdots$  Cg2 distance and acute C–Cl···Cg2 angle, this interaction is only weak.



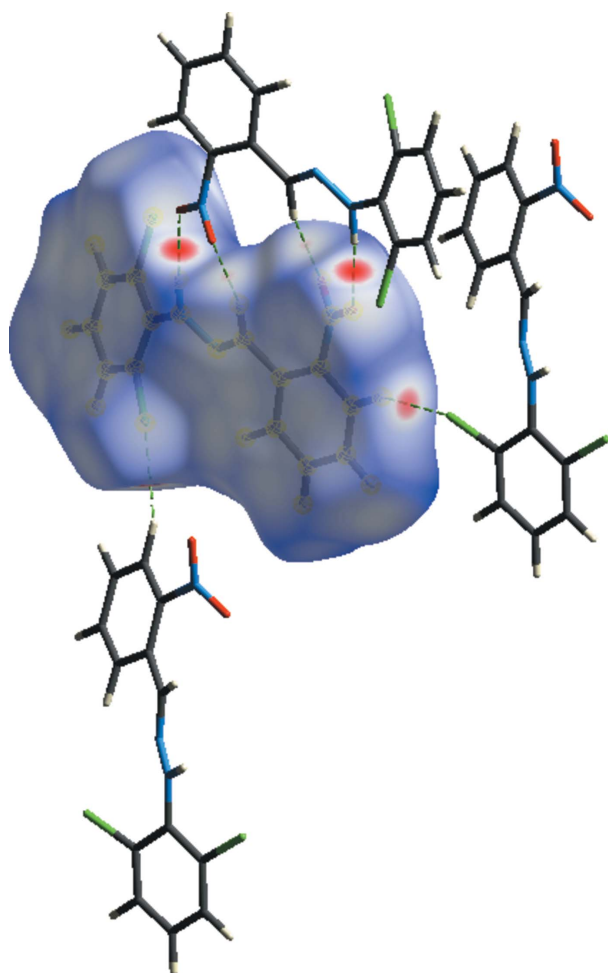
**Figure 4**

A general view of the crystal packing along the *a* axis of the title compound. Dashed lines indicate the intramolecular N–H···Cl, C–H···O, intermolecular N–H···O, C–H···Cl interactions and Cl···H, O···H contacts. [Symmetry codes: (a)  $x, 1 + y, z$ ; (b)  $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ ; (c)  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (d)  $x, -1 + y, z$ ; (e)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (f)  $1 - x, 1 - y, 1 - z$ ; (g)  $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$ ; (h)  $1 - x, -y, 1 - z$ ].


**Figure 5**

A general view of the crystal packing with the hydrogen bonds and contacts along the  $b$  axis of the title compound, forming pairs of hydrogen-bonded molecular layers parallel to  $(020)$ .

Hirshfeld surface analysis was used to analyse the various intermolecular interactions in the title compound, through mapping the normalized contact distance ( $d_{\text{norm}}$ ) using *CystalExplorer* (Turner *et al.*, 2017; Spackman & Jayatilaka, 2009). The Hirshfeld surface mapped over  $d_{\text{norm}}$  using a standard surface resolution with a fixed colour scale of  $-0.1980$  (red) to


**Figure 6**

A view of the Hirshfeld surface mapped for the title compound over  $d_{\text{norm}}$  in the range  $-0.1980$  to  $1.3500$  arbitrary units.

**Table 1**

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

$Cg2$  is the centroid of the  $C8-C13$  ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots Cl1$	0.95	2.48	2.939 (2)	110
$N1-H1N\cdots O2^i$	0.95	2.40	3.327 (3)	166
$C7-H7A\cdots O1$	0.93	2.34	2.774 (4)	108
$C12-H12A\cdots Cl2^{ii}$	0.93	2.80	3.679 (3)	157
$C2-Cl1\cdots Cg2^{iii}$	1.73 (1)	3.90 (1)	3.511 (3)	64 (1)

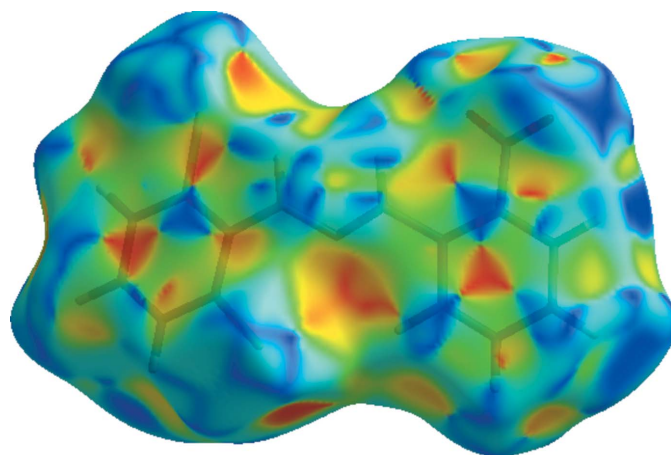
Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$ ; (iii)  $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$ .

**Table 2**

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

Contact	Distance	Symmetry operation
$Cl1\cdots H11A$	3.06	$x, 1+y, z$
$C2\cdots C8$	3.464 (4)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
$H1N\cdots O2$	2.40	$1-x, 1-y, 1-z$
$O1\cdots H4A$	2.68	$\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$
$Cl2\cdots H12A$	2.80	$-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
$N3\cdots C4$	3.447 (4)	$\frac{3}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$

$1.3500$  (blue) a.u. is shown in Fig. 6. The white surface indicates contacts with distances equal to the sum of van der Waals radii, and the red and blue colours indicate distances shorter (in close contact) or longer (distant contact) than the van der Waals radii, respectively (Venkatesan *et al.*, 2016). The dark-red spots on the  $d_{\text{norm}}$  surface arise as a result of short interatomic contacts (Table 2), while the other weaker intermolecular interactions appear as light-red spots. The red points, which represent closer contacts and negative  $d_{\text{norm}}$  values on the surface, correspond to the  $C-H\cdots O$  and  $C-H\cdots Cl$  interactions. The shape-index of the Hirshfeld surface is a tool for visualizing the  $\pi$ - $\pi$  stacking by the presence of adjacent red and blue triangles; if there are no such triangles, then there are no  $\pi$ - $\pi$  interactions. The plot of the Hirshfeld surface mapped over shape-index shown in Fig. 7 clearly suggests that there are  $\pi$ - $\pi$  interactions in the crystal packing of the title compound.


**Figure 7**

View of the three-dimensional Hirshfeld surface of the title compound plotted over shape-index.

**Table 3**

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

Contact	Percentage contribution
H···H	23.0
O···H/H···O	20.1
Cl···H/H···Cl	19.0
C···C	11.2
H···C/C···H	8.0
N···H/H···N	5.5
Cl···Cl	3.3
N···C/C···N	3.1
Cl···C/C···Cl	3.0
O···C/C···O	1.4
Cl···O/O···Cl	1.3
Cl···N/N···Cl	0.8
O···O	0.2
O···N/N···O	0.1

The percentage contributions of various contacts to the total Hirshfeld surface are listed in Table 3 and shown in the two-dimensional fingerprint plots in Fig. 8. As revealed by the two-dimensional fingerprint plots (Fig. 8), the crystal packing is dominated by H···H contacts, representing van der Waals interactions (23.0% contribution to the overall surface), followed by O···H and Cl···H interactions, which contribute 20.1% and 19.0%, respectively.

#### 4. Database survey

Six compounds closely resemble the title compound, *viz.* 1-(2,4-dinitrophenyl)-2-[(*E*)-(3,4,5-trimethoxybenzylidene)hydrazine] (CSD refcode GISJAV; Chantrapromma *et al.*, 2014), (*E*)-1-(2,4-dinitrophenyl)-2-[1-(3-methoxyphenyl)ethylidene]hydrazine (XEBCEO; Fun *et al.*, 2012), 1-(2,4-dinitrophenyl)-2-[(*E*)-2,4,5-trimethoxybenzylidene]hydrazine (AFUSEB; Fun *et al.*, 2013), (*E*)-1-(2,4-dinitrophenyl)-2-(1-(2-methoxyphenyl)ethylidene)hydrazine (OBUJAY; Fun *et al.*, 2011), (*E*)-1-(2,4-dinitrophenyl)-2-[1-(3-fluorophenyl)ethylidene]hydrazine (PAVKAA; Chantrapromma *et al.*, 2012) and (*E*)-1-(2,4-dinitrophenyl)-2-[1-(2-nitrophenyl)ethylidene]hydrazine (YAHRUW; Nilwanna *et al.*, 2011). All bond lengths (Allen *et al.*, 1987) and angles for the title compound are within normal ranges and are comparable to those observed in these structures. In each one, the configuration of the imine C=N bond is *E*.

#### 5. Synthesis and crystallization

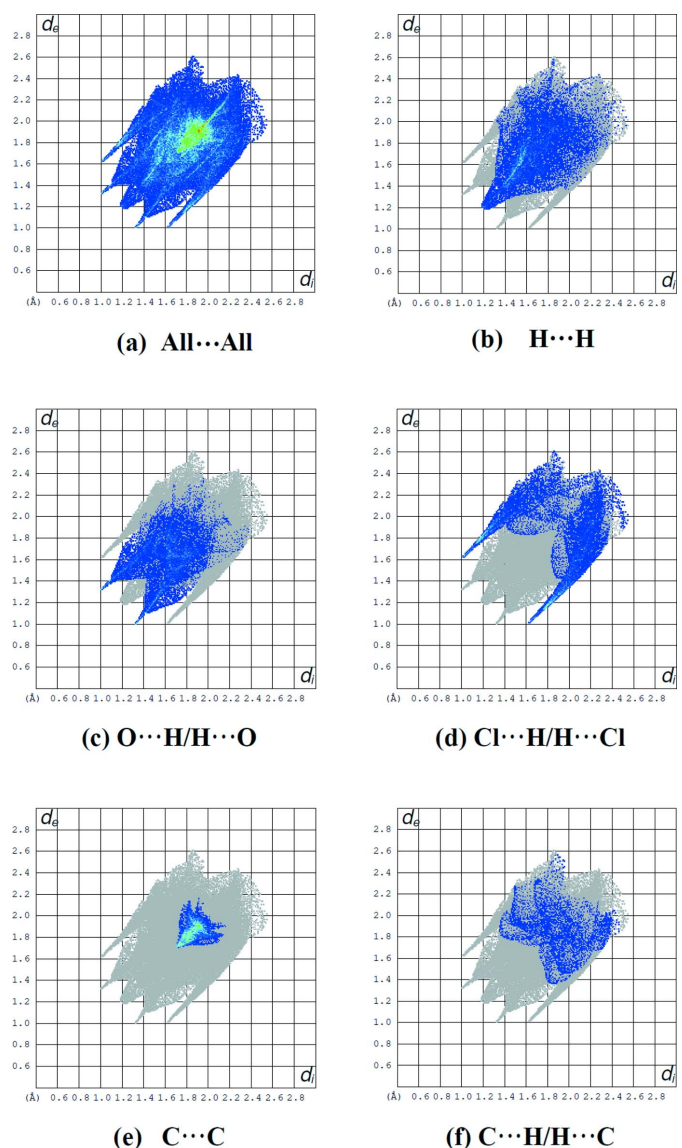
The title compound was synthesized according to the reported method (Atioğlu *et al.*, 2019; Maharramov *et al.*, 2018; Shixaliyev *et al.*, 2018, 2019). A mixture of 2-nitrobenzaldehyde (10 mmol), CH<sub>3</sub>COONa (0.82 g), ethanol (50 mL) and (2,6-dichlorophenyl)hydrazine (10.2 mmol) was refluxed at 353 K under stirring for 2 h. The reaction mixture was cooled to room temperature and water (50 mL) was added to give a precipitate of the crude product, which was filtered off, washed with diluted ethanol (1:1 with water) and dried *in vacuo* using

a rotary evaporator. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

Title compound: orange solid (90%); m.p. 398 K. Analysis calculated for C<sub>13</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub> (*M* = 310.13): C 50.35, H 2.93, N 13.55; found: C 50.27, H 2.86, N 13.54%. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 10.20 (1H, -NH), 8.41 (1H, -CH), 7.13–8.08 (7H, aromatic). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): δ 147.47, 137.80, 133.76, 133.32, 130.17, 129.85, 129.16, 128.00, 127.08, 125.86, 124.96. ESI-MS: *m/z*: 311.08 [*M*+H]<sup>+</sup>.

#### 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were refined using a riding model with *d*(C–H) = 0.93 Å, *d*(N–H) = 0.95 Å and *U*<sub>iso</sub> = 1.2*U*<sub>eq</sub>(N,C).



**Figure 8**  
(a) The full two-dimensional fingerprint plot for the title compound and (b)–(f) those delineated into H···H, O···H/H···O, Cl···H/H···Cl, C···C and C···H/H···C contacts, respectively.

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>13</sub> H <sub>9</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>2</sub>
<i>M</i> <sub>r</sub>	310.13
Crystal system, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.1138 (4), 12.6827 (6), 15.1613 (8)
$\beta$ (°)	100.571 (2)
<i>V</i> (Å <sup>3</sup> )	1344.67 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.49
Crystal size (mm)	0.26 × 0.22 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2003)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.868, 0.906
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	22007, 2521, 2184
<i>R</i> <sub>int</sub>	0.057
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.617
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.052, 0.118, 1.07
No. of reflections	2521
No. of parameters	181
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.32, -0.40

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

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## supporting information

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## Crystal structure and Hirshfeld surface analysis of (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine

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### Computing details

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, 2020).

### (*E*)-1-(2,6-Dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine

#### Crystal data

$C_{13}H_9Cl_2N_3O_2$

$M_r = 310.13$

Monoclinic,  $P2_1/n$

$a = 7.1138$  (4) Å

$b = 12.6827$  (6) Å

$c = 15.1613$  (8) Å

$\beta = 100.571$  (2)°

$V = 1344.67$  (12) Å<sup>3</sup>

$Z = 4$

$F(000) = 632$

$D_x = 1.532$  Mg m<sup>-3</sup>

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

Cell parameters from 9979 reflections

$\theta = 2.7\text{--}27.9^\circ$

$\mu = 0.49$  mm<sup>-1</sup>

$T = 296$  K

Plate, orange

$0.26 \times 0.22 \times 0.18$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

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

$T_{\min} = 0.868$ ,  $T_{\max} = 0.906$

22007 measured reflections

2521 independent reflections

2184 reflections with  $I > 2\sigma(I)$

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

$\theta_{\max} = 26.0^\circ$ ,  $\theta_{\min} = 2.7^\circ$

$h = -8 \rightarrow 8$

$k = -15 \rightarrow 15$

$l = -18 \rightarrow 18$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.118$

$S = 1.07$

2521 reflections

181 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 1.7039P]$

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

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

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.40 \text{ e } \text{\AA}^{-3}$$

### 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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.48623 (11)	0.84495 (6)	0.29065 (5)	0.0562 (2)
Cl2	0.26473 (16)	0.52094 (7)	0.06054 (6)	0.0807 (3)
O1	0.7013 (4)	0.44141 (18)	0.49042 (15)	0.0702 (7)
O2	0.6516 (4)	0.2943 (2)	0.55110 (15)	0.0863 (8)
N1	0.4068 (4)	0.62149 (17)	0.24789 (15)	0.0473 (6)
H1N	0.396165	0.657432	0.301808	0.057*
N2	0.4727 (3)	0.52096 (16)	0.24606 (15)	0.0419 (5)
N3	0.6564 (3)	0.3486 (2)	0.48539 (15)	0.0509 (6)
C1	0.3930 (4)	0.6850 (2)	0.17229 (17)	0.0405 (6)
C2	0.4275 (4)	0.7938 (2)	0.18315 (18)	0.0410 (6)
C3	0.4131 (4)	0.8620 (2)	0.1116 (2)	0.0530 (7)
H3A	0.435083	0.933692	0.121363	0.064*
C4	0.3661 (5)	0.8234 (3)	0.0258 (2)	0.0623 (9)
H4A	0.359130	0.868645	-0.023006	0.075*
C5	0.3296 (4)	0.7177 (3)	0.0122 (2)	0.0594 (8)
H5A	0.298464	0.691722	-0.046044	0.071*
C6	0.3384 (4)	0.6497 (2)	0.08380 (19)	0.0487 (7)
C7	0.4904 (4)	0.4688 (2)	0.31903 (18)	0.0414 (6)
H7A	0.467933	0.500896	0.371280	0.050*
C8	0.5469 (4)	0.35755 (19)	0.31939 (17)	0.0377 (5)
C9	0.5193 (4)	0.3022 (2)	0.23815 (19)	0.0468 (6)
H9A	0.473272	0.337842	0.184977	0.056*
C10	0.5589 (4)	0.1961 (2)	0.2353 (2)	0.0565 (8)
H10A	0.541762	0.161493	0.180264	0.068*
C11	0.6239 (4)	0.1405 (2)	0.3132 (2)	0.0586 (8)
H11A	0.649659	0.068772	0.310822	0.070*
C12	0.6501 (4)	0.1916 (2)	0.3942 (2)	0.0515 (7)
H12A	0.691729	0.154697	0.447219	0.062*
C13	0.6139 (4)	0.2987 (2)	0.39640 (17)	0.0396 (6)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0685 (5)	0.0450 (4)	0.0534 (4)	-0.0010 (3)	0.0064 (3)	-0.0065 (3)
Cl2	0.1061 (8)	0.0636 (5)	0.0648 (5)	-0.0150 (5)	-0.0046 (5)	-0.0194 (4)
O1	0.0956 (18)	0.0501 (13)	0.0590 (14)	-0.0025 (12)	-0.0014 (12)	-0.0147 (11)
O2	0.130 (2)	0.0877 (18)	0.0400 (12)	-0.0075 (17)	0.0109 (13)	0.0151 (12)



N1	0.0694 (16)	0.0337 (11)	0.0405 (12)	0.0096 (10)	0.0143 (11)	0.0029 (9)
N2	0.0482 (13)	0.0343 (11)	0.0444 (12)	0.0006 (9)	0.0112 (10)	0.0012 (9)
N3	0.0540 (14)	0.0554 (15)	0.0415 (13)	0.0043 (11)	0.0042 (11)	0.0005 (11)
C1	0.0391 (13)	0.0418 (14)	0.0398 (13)	0.0053 (11)	0.0053 (11)	0.0044 (11)
C2	0.0384 (13)	0.0408 (13)	0.0440 (14)	0.0039 (11)	0.0077 (11)	0.0041 (11)
C3	0.0544 (17)	0.0450 (16)	0.0610 (18)	0.0080 (13)	0.0140 (14)	0.0148 (14)
C4	0.064 (2)	0.071 (2)	0.0523 (18)	0.0132 (16)	0.0128 (15)	0.0224 (16)
C5	0.0589 (19)	0.079 (2)	0.0383 (15)	0.0090 (16)	0.0042 (13)	0.0023 (15)
C6	0.0492 (16)	0.0520 (16)	0.0427 (15)	0.0016 (13)	0.0023 (12)	-0.0015 (13)
C7	0.0481 (15)	0.0363 (13)	0.0414 (14)	0.0031 (11)	0.0120 (11)	-0.0008 (11)
C8	0.0381 (13)	0.0366 (13)	0.0398 (13)	-0.0018 (10)	0.0110 (10)	-0.0004 (10)
C9	0.0527 (16)	0.0465 (15)	0.0421 (14)	0.0006 (12)	0.0111 (12)	-0.0035 (12)
C10	0.0641 (19)	0.0477 (16)	0.0602 (19)	-0.0038 (14)	0.0178 (15)	-0.0190 (15)
C11	0.0602 (19)	0.0317 (14)	0.085 (2)	-0.0011 (13)	0.0175 (17)	-0.0048 (15)
C12	0.0545 (17)	0.0377 (14)	0.0615 (18)	0.0005 (12)	0.0089 (14)	0.0091 (13)
C13	0.0401 (13)	0.0374 (13)	0.0415 (14)	-0.0018 (10)	0.0078 (11)	-0.0008 (11)

*Geometric parameters (Å, °)*

C11—C2	1.732 (3)	C4—H4A	0.9300
C12—C6	1.731 (3)	C5—C6	1.380 (4)
O1—N3	1.218 (3)	C5—H5A	0.9300
O2—N3	1.217 (3)	C7—C8	1.467 (3)
N1—N2	1.361 (3)	C7—H7A	0.9300
N1—C1	1.390 (3)	C8—C13	1.394 (4)
N1—H1N	0.9510	C8—C9	1.400 (4)
N2—C7	1.275 (3)	C9—C10	1.377 (4)
N3—C13	1.471 (3)	C9—H9A	0.9300
C1—C6	1.400 (4)	C10—C11	1.381 (5)
C1—C2	1.406 (4)	C10—H10A	0.9300
C2—C3	1.376 (4)	C11—C12	1.371 (4)
C3—C4	1.374 (4)	C11—H11A	0.9300
C3—H3A	0.9300	C12—C13	1.384 (4)
C4—C5	1.374 (5)	C12—H12A	0.9300
N2—N1—C1	119.9 (2)	C5—C6—C12	117.5 (2)
N2—N1—H1N	123.3	C1—C6—C12	121.2 (2)
C1—N1—H1N	115.2	N2—C7—C8	119.0 (2)
C7—N2—N1	116.6 (2)	N2—C7—H7A	120.5
O2—N3—O1	122.8 (3)	C8—C7—H7A	120.5
O2—N3—C13	118.4 (3)	C13—C8—C9	116.1 (2)
O1—N3—C13	118.7 (2)	C13—C8—C7	124.7 (2)
N1—C1—C6	124.7 (2)	C9—C8—C7	119.0 (2)
N1—C1—C2	119.2 (2)	C10—C9—C8	121.4 (3)
C6—C1—C2	116.0 (2)	C10—C9—H9A	119.3
C3—C2—C1	122.6 (3)	C8—C9—H9A	119.3
C3—C2—C11	118.5 (2)	C9—C10—C11	120.6 (3)
C1—C2—C11	119.0 (2)	C9—C10—H10A	119.7

C4—C3—C2	119.6 (3)	C11—C10—H10A	119.7
C4—C3—H3A	120.2	C12—C11—C10	119.7 (3)
C2—C3—H3A	120.2	C12—C11—H11A	120.2
C5—C4—C3	119.8 (3)	C10—C11—H11A	120.2
C5—C4—H4A	120.1	C11—C12—C13	119.3 (3)
C3—C4—H4A	120.1	C11—C12—H12A	120.3
C4—C5—C6	120.8 (3)	C13—C12—H12A	120.3
C4—C5—H5A	119.6	C12—C13—C8	122.8 (3)
C6—C5—H5A	119.6	C12—C13—N3	115.9 (3)
C5—C6—C1	121.2 (3)	C8—C13—N3	121.3 (2)
C1—N1—N2—C7	176.7 (2)	N2—C7—C8—C13	164.3 (3)
N2—N1—C1—C6	37.1 (4)	N2—C7—C8—C9	-20.8 (4)
N2—N1—C1—C2	-145.8 (2)	C13—C8—C9—C10	-0.8 (4)
N1—C1—C2—C3	-178.8 (2)	C7—C8—C9—C10	-176.0 (3)
C6—C1—C2—C3	-1.4 (4)	C8—C9—C10—C11	1.3 (5)
N1—C1—C2—C11	0.1 (3)	C9—C10—C11—C12	-0.3 (5)
C6—C1—C2—C11	177.4 (2)	C10—C11—C12—C13	-1.1 (5)
C1—C2—C3—C4	-1.0 (4)	C11—C12—C13—C8	1.6 (4)
C11—C2—C3—C4	-179.8 (2)	C11—C12—C13—N3	-176.6 (3)
C2—C3—C4—C5	1.5 (5)	C9—C8—C13—C12	-0.7 (4)
C3—C4—C5—C6	0.3 (5)	C7—C8—C13—C12	174.3 (3)
C4—C5—C6—C1	-2.9 (5)	C9—C8—C13—N3	177.4 (2)
C4—C5—C6—C12	173.1 (3)	C7—C8—C13—N3	-7.7 (4)
N1—C1—C6—C5	-179.5 (3)	O2—N3—C13—C12	-26.1 (4)
C2—C1—C6—C5	3.3 (4)	O1—N3—C13—C12	151.3 (3)
N1—C1—C6—C12	4.7 (4)	O2—N3—C13—C8	155.7 (3)
C2—C1—C6—C12	-172.5 (2)	O1—N3—C13—C8	-26.9 (4)
N1—N2—C7—C8	175.4 (2)		

*Hydrogen-bond geometry (Å, °)*

Cg2 is the centroid of the C8—C13 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>
N1—H1 <i>N</i> ...C11	0.95	2.48	2.939 (2)	110
N1—H1 <i>N</i> ...O2 <sup>i</sup>	0.95	2.40	3.327 (3)	166
C7—H7 <i>A</i> ...O1	0.93	2.34	2.774 (4)	108
C12—H12 <i>A</i> ...C12 <sup>ii</sup>	0.93	2.80	3.679 (3)	157
C2—C11...Cg2 <sup>iii</sup>	1.73 (1)	3.90 (1)	3.511 (3)	64 (1)

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