

(*E*)-1-(2,6-Dichlorophenyl)-2-(3-nitrobenzylidene)hydrazine: crystal structure and Hirshfeld surface analysis

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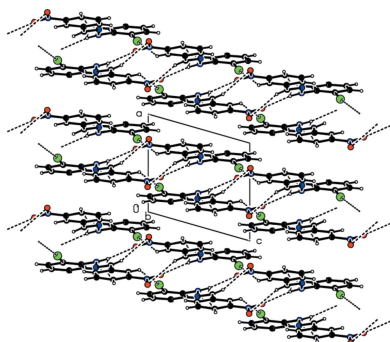
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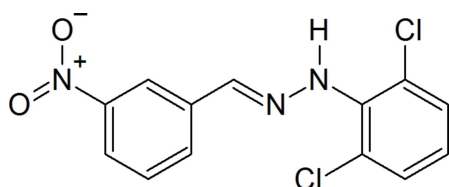
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The stabilized conformation of the title compound, C₁₃H₉Cl₂N₃O₂, is similar to that of the isomeric compound (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine. The 2,6-dichlorophenyl ring and the nitro-substituted benzene ring form a dihedral angle of 26.25 (16)°. In the crystal, face-to-face π - π stacking interactions along the *a*-axis direction occur between the centroids of the 2,6-dichlorophenyl ring and the nitro-substituted benzene ring. The molecules are further linked by C—H···O contacts and N—H···O and C—H···Cl hydrogen bonds, forming pairs of hydrogen-bonded molecular layers parallel to (100). The Hirshfeld surface analysis of the crystal structure indicates that the most important contributions to the crystal packing are from H···H (22.1%), Cl···H/H···Cl (20.5%), O···H/H···O (19.7%), C···C (11.1%) and C···H/H···C (8.3%) interactions.

1. Chemical context

Schiff bases as well as hydrazone ligands and their complexes have attracted much attention because of their high synthetic potential for organic and inorganic chemistry and their diverse useful properties (Maharramov *et al.*, 2018; Mahmudov *et al.*, 2014). The analytical and catalytic properties of this class of compounds are strongly dependent on the groups attached to the hydrazone moiety (Shixaliyev *et al.*, 2019). On the other hand, intermolecular interactions organize molecular architectures, which play a critical role in synthesis, catalysis, micellization, *etc* (Akbari *et al.*, 2017; Gurbanov *et al.*, 2018; Mahmoudi *et al.*, 2018 and references cited therein). New types of weak interactions such as halogen, chalcogen, pnictogen and tetrel bonds or their cooperation with hydrogen bonds are able to drive the synthesis and catalysis, as well as improve properties of materials (Mizar *et al.*, 2012; Mahmudov *et al.*, 2019 and references cited therein). For that, the main skeleton of the arylhydrazone ligand should be extended with weak bond-donor centre(s). In order to continue our work in this perspective, we have functionalized a new azo dye, (*E*)-1-(2,6-dichlorophenyl)-2-(3-nitrobenzylidene)hydrazine, (I), 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 $26.25(16)^\circ$, while the nitro group is skewed out of the attached benzene ring plane by $6.3(2)^\circ$. The conformation is stabilized by an intramolecular N1–H1N···Cl1 interaction, which forms an *S*(6) graph-set motif (Table 1). The conformation of the title compound can be compared with that of the isomeric compound (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine (CSD refcode KUWG0B; Çelikesir *et al.*, 2020). Fig. 2 shows the overlay of the two isomers. The r.m.s. deviation of the overlay between the two isomers is 0.003 \AA . In the 2-nitro isomer, the dihedral angles are $21.16(14)^\circ$ (between the phenyl rings) and $27.06(18)^\circ$ (between the nitro group and the phenyl ring). The difference in angles may be due to the steric interaction resulting from the position

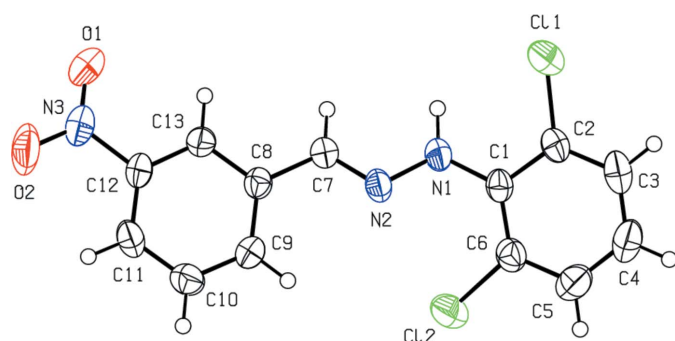


Figure 1
The molecular structure of the title compound, showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

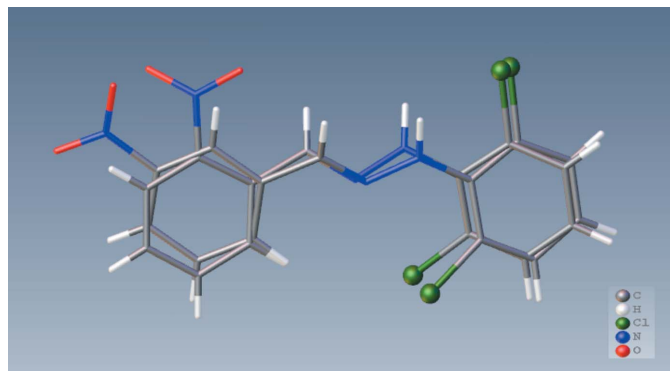


Figure 2
Overlay of the title compound and the isomer (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine (Çelikesir *et al.*, 2020).

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

<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–H1N···Cl1	0.95	2.54	2.940 (2)	106
N1–H1N···O1 ⁱ	0.95	2.31	3.243 (3)	168

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

of the nitro group on the benzene ring to which it is attached. The C11–C2–C1–N1, C12–C6–C1–N1, C2–C1–N1–N2, C1–N1–N2–C7, N1–N2–C7–C8, N2–C7–C8–C13, N2–C7–C8–C9, C8–C13–C12–N3, C13–C12–N3–O1 and C13–C12–N3–O2 torsion angles are $-0.1(4)$, $3.4(4)$, $-147.1(3)$, $177.3(3)$, $178.2(2)$, $165.5(3)$, $-15.6(4)$, $178.8(3)$, $6.2(4)$ and $-174.4(3)^\circ$, respectively.

3. Supramolecular features

In the crystal, face-to-face π – π stacking interactions [$Cg1 \cdots Cg2(-x, -\frac{1}{2} + y, 1 - z) = 3.753(2) \text{ \AA}$ with slippage of 1.380 \AA and $Cg1 \cdots Cg2(1 - x, -\frac{1}{2} + y, 1 - z) = 3.761(2) \text{ \AA}$ with slippage of 1.423 \AA , where *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C8–C13 rings, respectively] occur between the 2,6-dichlorophenyl ring and the nitro-substituted benzene ring of the title molecule along the *a*-axis direction (Fig. 3). The molecules are further linked by C–H···O contacts and N–

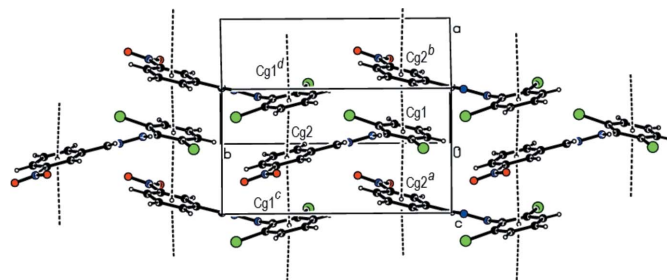


Figure 3
A view of the π – π stacking interactions of the title compound. *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C8–C13 benzene rings, respectively. [Symmetry codes: (a) $-x, -\frac{1}{2} + y, 1 - z$; (b) $1 - x, -\frac{1}{2} + y, 1 - z$; (c) $-x, \frac{1}{2} + y, 1 - z$; (d) $1 - x, \frac{1}{2}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

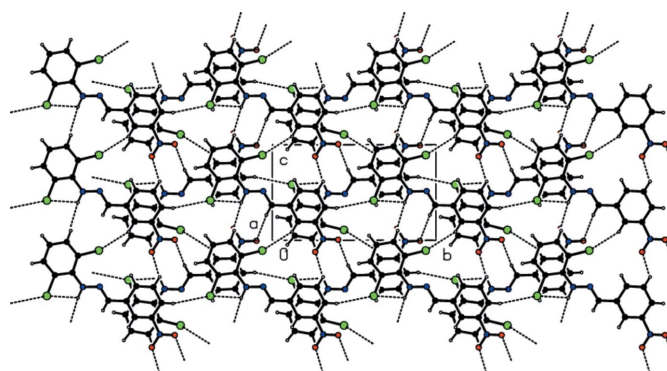


Figure 4
A general view of the crystal packing of the title compound along the *a* axis with hydrogen bonds and contacts shown as dashed lines.

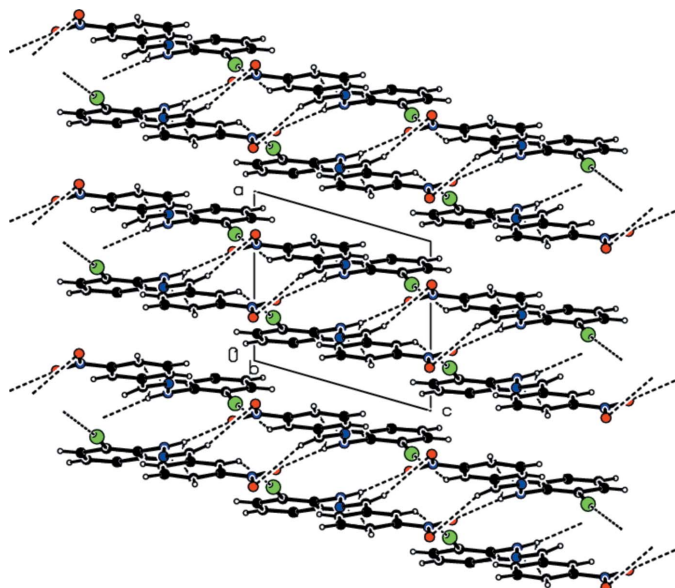


Figure 5
A general view of the crystal packing of the title compound along the *b* axis showing the pairs of hydrogen-bonded molecular layers parallel to (100).

H \cdots O and C–H \cdots Cl hydrogen bonds, forming pairs of hydrogen-bonded molecular layers parallel to (100) (Tables 1 and 2; Figs. 4 and 5). In the crystal, a C–Cl \cdots π interaction is also observed [C2–Cl1 \cdots Cg2 ($-x, -\frac{1}{2} + y, 1 - z$) = 3.9373 (18) Å, C2–Cl1 \cdots Cg2 = 62.59 (10) $^\circ$, where Cg2 is the centroid of the C8–C13 ring]. The large Cl \cdots Cg2 distance and acute C–Cl \cdots Cg2 angle, however, indicate that this interaction is only weak.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon, *et al.*, 2007) were performed with *Crystal Explorer17* (Turner *et al.*, 2017) to investigate the intermolecular interactions and surface morphology. The Hirshfeld surface mapped over d_{norm} in the range -0.2694 to 1.2224 a.u. and corresponding colours from red (shorter distance than the sum of van der Waals radii) over white to blue (longer distance

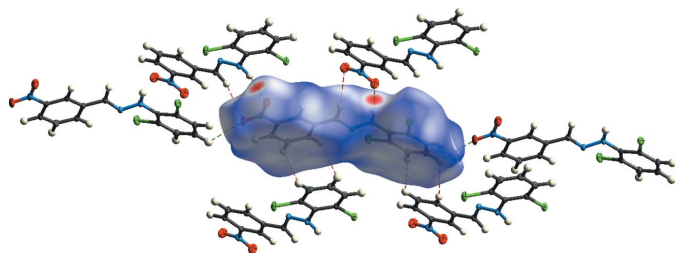


Figure 6
A view of the Hirshfeld surface mapped over d_{norm} in the range -0.2694 to 1.2224 arbitrary units showing C–H \cdots O, N–H \cdots O hydrogen bonds and H \cdots H interactions (van der Waals interactions). Applied colours for atoms: grey = C, white = H, blue = N, red = O and green = Cl.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
Cl1 \cdots H11A	3.13	$x, -1 + y, z$
H1N \cdots O1	2.31	$1 - x, -\frac{1}{2} + y, 2 - z$
H7A \cdots O2	2.77	$1 - x, -\frac{1}{2} + y, 2 - z$
C1 \cdots C11	3.405	$-x, -\frac{1}{2} + y, 1 - z$
Cl2 \cdots H13A	2.95	$x, y, -1 + z$
O2 \cdots H4A	2.66	$x, 1 + y, 1 + z$
C2 \cdots C8	3.426	$1 - x, -\frac{1}{2} + y, 1 - z$
H5A \cdots H10A	2.55	$-x, -\frac{1}{2} + y, -z$

than the sum of van der Waals radii) is shown in Fig. 6. The red points, which represent closer contacts and negative d_{norm} values on the surface, correspond to the N–H \cdots O, C–H \cdots O and C–H \cdots Cl interactions (Table 2). The shape-index of the Hirshfeld surface is a tool for visualizing the π – π stacking by the presence of adjacent red and blue triangles. The plot of the Hirshfeld surface mapped over shape-index shown in Fig. 7 clearly suggests that there are π – π interactions in the title compound.

In the crystal there are four major types of interaction (H \cdots H = 22.1%, Cl \cdots H = 20.5%, O \cdots H = 19.7%, C \cdots C = 11.1%) on the d_{norm} surface. The two-dimensional fingerprint plots are shown in Fig. 8. The interaction sequence of d_{norm} on the two-dimensional fingerprint plot (H \cdots H) > (Cl \cdots H) > (O \cdots H) > (C \cdots C) represents the nature of the packing in the crystal structure. The contribution of these major interactions governs the overall packing of crystal structure. The percentage contributions of other weak interactions are: C \cdots H/H \cdots C (8.3%), N \cdots H/H \cdots N (4.9%), Cl \cdots C/C \cdots Cl (3.3%), N \cdots C/C \cdots N (2.9%), Cl \cdots O/O \cdots Cl (2.6%), Cl \cdots N/N \cdots Cl (1.8%), C \cdots O/O \cdots C (1.7%) and Cl \cdots Cl (1.2%).

5. Database survey

A search of the Cambridge Structural Database (CSD version 5.40, update of September 2019; Groom *et al.*, 2016) gave only seven entries closely resembling the title compound. Our

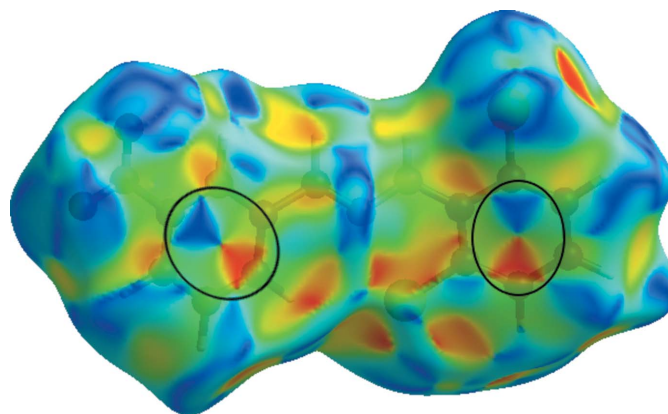


Figure 7
View of the three-dimensional Hirshfeld surfaces of the title compound plotted over shape-index.

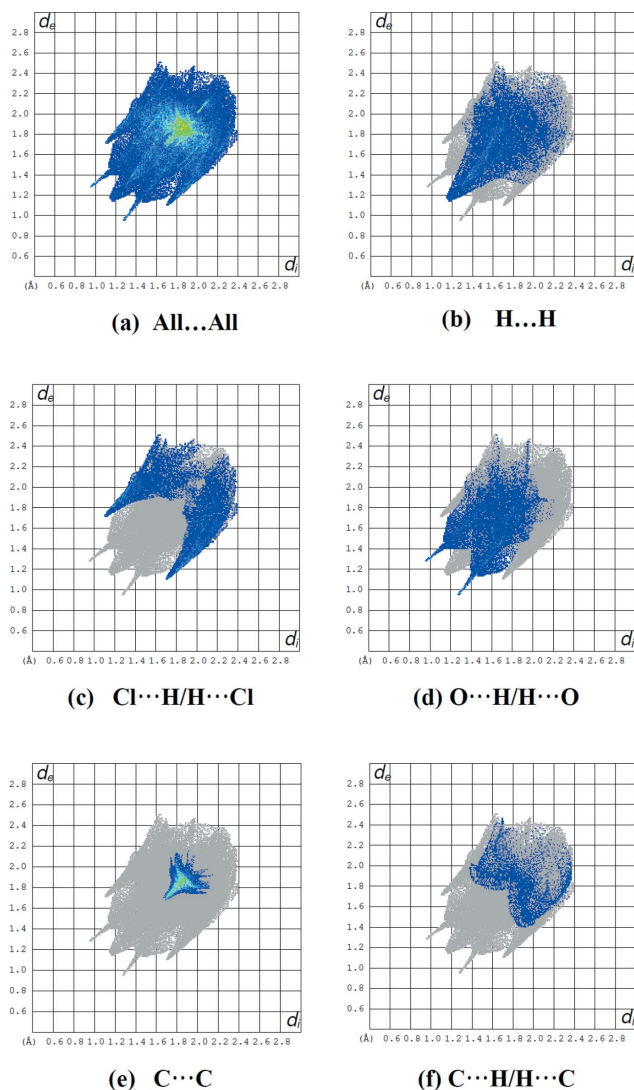


Figure 8
 (a) The full two-dimensional fingerprint plot for the title compound and (b)–(f) those delineated into H···H (22.1%), Cl···H/H···Cl (20.5%), O···H/H···O (19.7%), C···C (11.1%) and C···H/H···C (8.3%) contacts, respectively.

recently published compound (*E*)-1-(2,6-dichlorophenyl)-2-(2-nitrobenzylidene)hydrazine (KUGOB: Çelikesir *et al.*, 2020) is an isomer of the title compound. The other six compounds are 1-(2,4-dinitrophenyl)-2-[(*E*)-(3,4,5-trimethoxybenzylidene)hydrazine] (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 and these related compounds are comparable and within normal ranges.

Table 3
 Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₉ Cl ₂ N ₃ O ₂
<i>M_r</i>	310.13
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.1212 (14), 12.711 (3), 7.6991 (16)
β (°)	105.940 (7)
<i>V</i> (Å ³)	670.1 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	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> _{min} , <i>T</i> _{max}	0.873, 0.902
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	22230, 2744, 2392
<i>R</i> _{int}	0.062
(sin θ/λ) _{max} (Å ⁻¹)	0.627
Refinement	
<i>R</i> [[<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.031, 0.064, 1.11
No. of reflections	2744
No. of parameters	181
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.15, −0.16
Absolute structure	Flack <i>x</i> determined using 1032 quotients [(<i>I</i> ⁺) − (<i>I</i> [−])] / [(<i>I</i> ⁺) + (<i>I</i> [−])] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.04 (3)

Computer programs: *APEX3* (Bruker, 2007), *SAINT* (Bruker, 2007), *SHELXT2016/6* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *OLEX2* (Dolomanov *et al.*, 2009), *PLATON* (Spek, 2020).

6. Synthesis and crystallization

The title compound was synthesized according to the reported method (Atioğlu *et al.*, 2019; Maharramov *et al.*, 2018). A mixture of 3-nitrobenzaldehyde (10 mmol), CH₃COONa (0.82 g), ethanol (50 mL) and (2,6-dichlorophenyl)hydrazine (10.2 mmol) was refluxed at 353 K with 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* of rotary evaporator. Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution; yellow solid; yield 95%; m.p. 423 K. Analysis calculated for C₁₃H₉Cl₂N₃O₂ (*M* = 310.13): C 50.35, H 2.93, N 13.55; found: C 50.32, H 2.90, N 13.47%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.95 (1H, −NH), 8.40 (1H, −CH), 7.00–8.20 (7H, aromatic). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 149.00, 138.01, 137.50, 136.05, 132.11, 130.50, 129.04, 128.23, 126.24, 123.16, 119.90. ESI-MS: *m/z*: 311.14 [*M*+H]⁺.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were refined using a

riding model with $d(\text{C}-\text{H}) = 0.93 \text{ \AA}$, $d(\text{N}-\text{H}) = 0.95 \text{ \AA}$ and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N,C})$.

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supporting information

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Computing details

Data collection: *APEX3* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (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) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *PLATON* (Spek, 2020).

(*E*)-1-(2,6-Dichlorophenyl)-2-(3-nitrobenzylidene)hydrazine

Crystal data

$C_{13}H_9Cl_2N_3O_2$

$M_r = 310.13$

Monoclinic, $P2_1$

$a = 7.1212$ (14) Å

$b = 12.711$ (3) Å

$c = 7.6991$ (16) Å

$\beta = 105.940$ (7)°

$V = 670.1$ (2) Å³

$Z = 2$

$F(000) = 316$

$D_x = 1.537$ Mg m⁻³

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

Cell parameters from 9800 reflections

$\theta = 2.8$ – 26.3 °

$\mu = 0.49$ mm⁻¹

$T = 296$ K

Plate, orange

$0.26 \times 0.22 \times 0.18$ mm

Data collection

Bruker APEXII CCD
diffractometer

φ and ω scans

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

$T_{\min} = 0.873$, $T_{\max} = 0.902$

22230 measured reflections

2744 independent reflections

2392 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.8$ °

$h = -8 \rightarrow 8$

$k = -15 \rightarrow 15$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.064$

$S = 1.11$

2744 reflections

181 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2 + 0.0759P]$

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

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

$$\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
1032 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.04 (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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.28649 (13)	0.12020 (5)	0.58310 (10)	0.0583 (2)
Cl2	0.28511 (15)	0.43809 (7)	0.10800 (12)	0.0666 (3)
O1	0.3919 (5)	0.7625 (2)	1.1215 (3)	0.0799 (8)
O2	0.2541 (5)	0.9024 (2)	0.9937 (4)	0.0848 (9)
N1	0.3362 (4)	0.34075 (17)	0.4897 (3)	0.0465 (6)
H1N	0.401372	0.310054	0.602708	0.056*
N2	0.2806 (3)	0.44380 (18)	0.4863 (3)	0.0397 (5)
N3	0.3101 (4)	0.8121 (2)	0.9871 (4)	0.0531 (7)
C1	0.2672 (4)	0.2769 (2)	0.3396 (4)	0.0365 (6)
C2	0.2365 (4)	0.1696 (2)	0.3645 (4)	0.0411 (7)
C3	0.1710 (5)	0.1009 (2)	0.2220 (4)	0.0543 (8)
H3A	0.152757	0.030205	0.243822	0.065*
C4	0.1330 (5)	0.1370 (3)	0.0483 (5)	0.0588 (9)
H4A	0.086569	0.091344	-0.048297	0.071*
C5	0.1641 (5)	0.2419 (3)	0.0174 (4)	0.0558 (8)
H5A	0.139312	0.266660	-0.100398	0.067*
C6	0.2322 (4)	0.3105 (2)	0.1614 (4)	0.0426 (7)
C7	0.3439 (5)	0.4963 (2)	0.6318 (4)	0.0413 (7)
H7A	0.421014	0.463484	0.734710	0.050*
C8	0.2957 (4)	0.6082 (2)	0.6376 (3)	0.0359 (6)
C9	0.2219 (5)	0.6675 (2)	0.4811 (4)	0.0433 (7)
H9A	0.201931	0.635668	0.368765	0.052*
C10	0.1784 (5)	0.7724 (2)	0.4908 (4)	0.0512 (8)
H10A	0.131772	0.810787	0.384850	0.061*
C11	0.2029 (5)	0.8214 (2)	0.6557 (4)	0.0475 (7)
H11A	0.169393	0.891678	0.662994	0.057*
C12	0.2790 (4)	0.7623 (2)	0.8092 (4)	0.0387 (6)
C13	0.3274 (4)	0.6576 (2)	0.8048 (4)	0.0375 (6)
H13A	0.380225	0.620594	0.911236	0.045*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0720 (6)	0.0433 (4)	0.0608 (5)	0.0025 (4)	0.0200 (4)	0.0100 (4)
Cl2	0.0988 (8)	0.0470 (4)	0.0610 (5)	0.0050 (5)	0.0339 (5)	0.0121 (4)

O1	0.122 (2)	0.0705 (17)	0.0406 (13)	0.0047 (16)	0.0118 (14)	-0.0139 (12)
O2	0.106 (2)	0.0565 (16)	0.0844 (19)	0.0181 (15)	0.0135 (16)	-0.0350 (14)
N1	0.0622 (17)	0.0308 (12)	0.0418 (13)	0.0081 (10)	0.0060 (11)	-0.0040 (9)
N2	0.0457 (13)	0.0285 (10)	0.0451 (12)	0.0019 (11)	0.0128 (10)	-0.0042 (10)
N3	0.0580 (18)	0.0489 (15)	0.0529 (16)	-0.0065 (13)	0.0163 (14)	-0.0188 (13)
C1	0.0341 (15)	0.0321 (12)	0.0434 (14)	0.0045 (11)	0.0110 (12)	-0.0048 (10)
C2	0.0420 (17)	0.0315 (13)	0.0513 (17)	0.0049 (12)	0.0153 (13)	-0.0011 (11)
C3	0.0538 (19)	0.0350 (16)	0.073 (2)	0.0013 (14)	0.0155 (16)	-0.0127 (15)
C4	0.059 (2)	0.055 (2)	0.0569 (19)	0.0011 (16)	0.0081 (15)	-0.0228 (15)
C5	0.058 (2)	0.066 (2)	0.0420 (17)	0.0124 (17)	0.0099 (15)	-0.0063 (14)
C6	0.0452 (18)	0.0368 (14)	0.0477 (16)	0.0057 (13)	0.0158 (14)	-0.0013 (13)
C7	0.0522 (19)	0.0326 (14)	0.0385 (15)	0.0020 (12)	0.0116 (13)	-0.0017 (11)
C8	0.0366 (14)	0.0336 (13)	0.0379 (13)	-0.0044 (12)	0.0108 (11)	-0.0043 (12)
C9	0.0506 (19)	0.0418 (16)	0.0354 (15)	-0.0022 (13)	0.0080 (13)	-0.0064 (11)
C10	0.059 (2)	0.0423 (16)	0.0455 (18)	0.0014 (15)	0.0033 (15)	0.0060 (13)
C11	0.0504 (19)	0.0295 (13)	0.0594 (19)	0.0028 (13)	0.0097 (15)	-0.0045 (13)
C12	0.0380 (15)	0.0361 (14)	0.0417 (16)	-0.0054 (12)	0.0104 (12)	-0.0109 (11)
C13	0.0422 (16)	0.0355 (13)	0.0355 (14)	-0.0025 (11)	0.0119 (12)	-0.0009 (10)

Geometric parameters (Å, °)

C11—C2	1.739 (3)	C4—H4A	0.9300
C12—C6	1.740 (3)	C5—C6	1.389 (4)
O1—N3	1.215 (4)	C5—H5A	0.9300
O2—N3	1.220 (4)	C7—C8	1.467 (4)
N1—N2	1.367 (3)	C7—H7A	0.9300
N1—C1	1.387 (3)	C8—C13	1.393 (3)
N1—H1N	0.9500	C8—C9	1.396 (4)
N2—C7	1.275 (3)	C9—C10	1.375 (4)
N3—C12	1.469 (3)	C9—H9A	0.9300
C1—C6	1.392 (4)	C10—C11	1.382 (4)
C1—C2	1.404 (4)	C10—H10A	0.9300
C2—C3	1.379 (4)	C11—C12	1.379 (4)
C3—C4	1.369 (5)	C11—H11A	0.9300
C3—H3A	0.9300	C12—C13	1.378 (4)
C4—C5	1.383 (5)	C13—H13A	0.9300
N2—N1—C1	120.7 (2)	C5—C6—C12	116.6 (2)
N2—N1—H1N	118.5	C1—C6—C12	121.8 (2)
C1—N1—H1N	119.7	N2—C7—C8	120.4 (3)
C7—N2—N1	117.0 (2)	N2—C7—H7A	119.8
O1—N3—O2	122.6 (3)	C8—C7—H7A	119.8
O1—N3—C12	119.0 (3)	C13—C8—C9	118.7 (2)
O2—N3—C12	118.5 (3)	C13—C8—C7	119.0 (2)
N1—C1—C6	124.6 (2)	C9—C8—C7	122.2 (2)
N1—C1—C2	119.2 (3)	C10—C9—C8	120.9 (3)
C6—C1—C2	116.1 (2)	C10—C9—H9A	119.5
C3—C2—C1	122.5 (3)	C8—C9—H9A	119.5

C3—C2—C11	118.4 (2)	C9—C10—C11	120.9 (3)
C1—C2—C11	119.0 (2)	C9—C10—H10A	119.6
C4—C3—C2	119.9 (3)	C11—C10—H10A	119.6
C4—C3—H3A	120.1	C12—C11—C10	117.5 (3)
C2—C3—H3A	120.1	C12—C11—H11A	121.2
C3—C4—C5	119.6 (3)	C10—C11—H11A	121.2
C3—C4—H4A	120.2	C13—C12—C11	123.2 (2)
C5—C4—H4A	120.2	C13—C12—N3	117.7 (3)
C4—C5—C6	120.3 (3)	C11—C12—N3	119.1 (2)
C4—C5—H5A	119.8	C12—C13—C8	118.7 (2)
C6—C5—H5A	119.8	C12—C13—H13A	120.7
C5—C6—C1	121.5 (3)	C8—C13—H13A	120.7
C1—N1—N2—C7	177.3 (3)	N1—N2—C7—C8	178.2 (2)
N2—N1—C1—C6	35.6 (4)	N2—C7—C8—C13	165.5 (3)
N2—N1—C1—C2	-147.1 (3)	N2—C7—C8—C9	-15.6 (4)
N1—C1—C2—C3	-179.0 (3)	C13—C8—C9—C10	-1.0 (4)
C6—C1—C2—C3	-1.5 (4)	C7—C8—C9—C10	-179.9 (3)
N1—C1—C2—C11	-0.1 (4)	C8—C9—C10—C11	-1.3 (5)
C6—C1—C2—C11	177.4 (2)	C9—C10—C11—C12	2.3 (5)
C1—C2—C3—C4	-0.2 (5)	C10—C11—C12—C13	-1.2 (4)
C11—C2—C3—C4	-179.1 (3)	C10—C11—C12—N3	179.1 (3)
C2—C3—C4—C5	1.2 (5)	O1—N3—C12—C13	6.2 (4)
C3—C4—C5—C6	-0.4 (5)	O2—N3—C12—C13	-174.4 (3)
C4—C5—C6—C1	-1.4 (5)	O1—N3—C12—C11	-174.0 (3)
C4—C5—C6—C12	175.0 (3)	O2—N3—C12—C11	5.4 (4)
N1—C1—C6—C5	179.6 (3)	C11—C12—C13—C8	-1.0 (4)
C2—C1—C6—C5	2.3 (4)	N3—C12—C13—C8	178.8 (3)
N1—C1—C6—C12	3.4 (4)	C9—C8—C13—C12	2.0 (4)
C2—C1—C6—C12	-173.9 (2)	C7—C8—C13—C12	-179.0 (3)

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>
N1—H1N···C11	0.95	2.54	2.940 (2)	106
N1—H1N···O1 ⁱ	0.95	2.31	3.243 (3)	168

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