



Crystal structure and Hirshfeld surface analysis of methyl 4-[(*E*)-2-(5-bromo-2-methoxybenzylidene)hydrazinyl]-3-nitrobenzoate

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The title compound, C₁₆H₁₄BrN₃O₅, is a novel halogen (Br) substituted hydrazine derivative. The hydrazine derivatives were the group of compounds with the general structure, R₁R₂C=NNH₂ (Uppal *et al.*, 2011), with the central RC=NNH₂ moiety bridging two different groups on both sides. An all-*trans* configuration of the backbone (RC=NNH₂) results in an extended molecular conformation. The dihedral angle between the 5-bromo-2-methoxyphenyl ring and the nitrophenyl ring is 4.4 (3)°. Intramolecular N–H···O interactions form *S*(6) graph-set motifs, while C–H···O and C–H···N interactions form *S*(5) graph-set motifs. Symmetry-related molecules are linked by C–H···O intermolecular interactions forming an R₂¹(10) graph-set motif. There are nearly face-to-face directional specific π–π stacking interactions between the centroids of the nitrophenyl ring and the benzene ring of the 5-bromo-2-methoxy group [centroid–centroid distance = 3.6121 (5) Å and slippage = 1.115 Å], which also contributes to the molecular packing. The Hirshfeld surface analysis was performed in order to visualize, explore and quantify the intermolecular interactions in the crystal lattice of the title compound.

1. Chemical context

Hydrazine and its derivatives have attracted much attention due to their synthetic potential for organic and inorganic chemical reactions and diverse useful properties (Levrant *et al.*, 2007; Li *et al.*, 2011). Hydrazine-based coupling methods are used in medical biotechnology to couple drugs to targeted antibodies, *e.g.* antibodies against a certain type of cancer cell (Wu *et al.*, 2005). Hydrazine possesses diverse biological and pharmacological properties, such as antimicrobial, anti-inflammatory, analgesic, antifungal, antitubercular, antiviral, anticancer, antiplatelet, antimalarial, anticonvulsant, cardioprotective, antihelminthic, antiprotozoal (Rollas & Küçükgül, 2007), antitrypanosomal and antischistosomiasis (Narang *et al.*, 2012). These compounds contain a C=N bond, which is conjugated with a lone pair of electrons of the functional N atom (Corey & Enders, 1976). The N atom of the hydrazine is nucleophilic and the C atom has both an electrophilic and a nucleophilic nature (Corey & Enders, 1976). The α-hydrogen of hydrazine is more potent than that of acidic ketones (Belskaya *et al.*, 2010). The combination of hydrazine with other functional groups results in new compounds with unique physical and chemical characteristics (Xavier *et al.*, 2012). Owing to their biological and pharmacological properties,

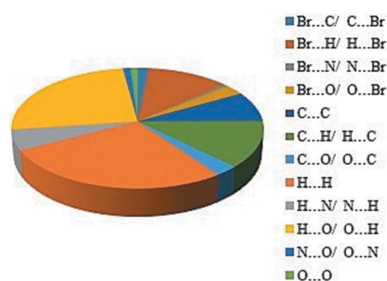
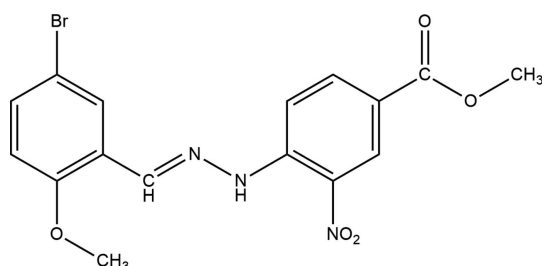


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots O4$	0.83	2.03	2.635 (3)	129
$C3-H3\cdots O1$	0.93	2.39	2.712 (4)	100
$C6-H6\cdots N3$	0.93	2.40	2.731 (4)	101
$C6-H6\cdots O4^i$	0.93	2.59	3.444 (5)	152
$C15-H15\cdots O4^i$	0.93	2.46	3.358 (4)	161

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

hydrazine derivatives play an important role for the synthesis of heterocyclic compounds (Banerjee *et al.*, 2009).



2. Structural commentary

Fig. 1 displays the title molecule with the atom-labelling scheme. Intramolecular $N2-H2A\cdots O4$ interactions form $S(6)$ graph-set motifs and $C3-H3\cdots O1$ and $C6-H6\cdots N3$ interactions form $S(5)$ graph-set motifs. The central bridging moiety $R_2C=NNHR_1$ adopts an all-*trans* conformation about the $C10-C9$, $C9-N3$, $N3-N2$ and $N2-C5$ bonds, with torsion angles of 176.0 (6), -178.1 (5), -177.0 (6) and 173.6 (6)°, leading to an extended molecular conformation, thereby causing the terminal bromomethoxyphenyl ring and nitrophenyl ring to occupy almost the same plane; the dihedral angle between the rings is 4.4 (3)°.

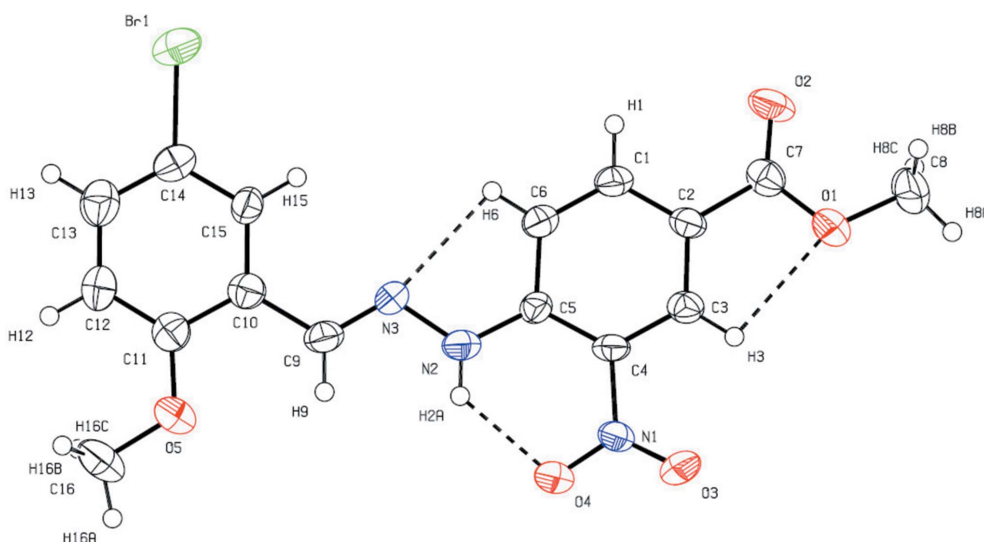


Figure 1
The molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

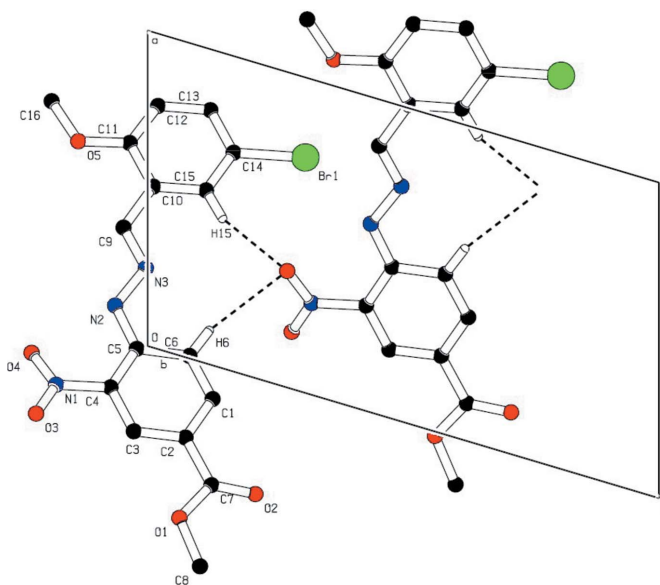


Figure 2
A view of part of the crystal structure of the title compound, showing the formation of $C-H\cdots O$ hydrogen bonds (dashed bonds).

3. Supramolecular features and Hirshfeld surface analysis

A significant number of weak $C-H\cdots O$, $C-H\cdots N$ and $N-H\cdots O$ intramolecular interactions and $C-H\cdots O$ intermolecular interactions (Table 1), along with direction-specific nearly face-to-face $\pi-\pi$ stacking interactions, are responsible for the stability of the molecular packing. Intermolecular $C-H\cdots O$ hydrogen-bond interactions forming $R_2^1(10)$ ring (Fig. 2). There are nearly face-to-face direction-specific $\pi-\pi$ stacking interactions between the centroids of the nitrophenyl ring (x, y, z) and the benzene ring of the 5-bromo-2-methoxy group ($x - 1, y, z$) [centroid-centroid distance = 3.6121 (5) Å

Table 2

Summary of the various contacts and their contributions to the Hirshfeld surface.

Contacts	Percentage contribution
Br...C/C...Br	1.6
Br...H/H...Br	11.7
Br...N/N...Br	0.7
Br...O/O...Br	2.8
C...C	8.1
C...H/H...C	12.5
C...O/O...C	2.7
H...H	27.2
H...N/N...H	5.5
H...O/O...H	25.1
N...O/O...N	1.1
O...O	1.0

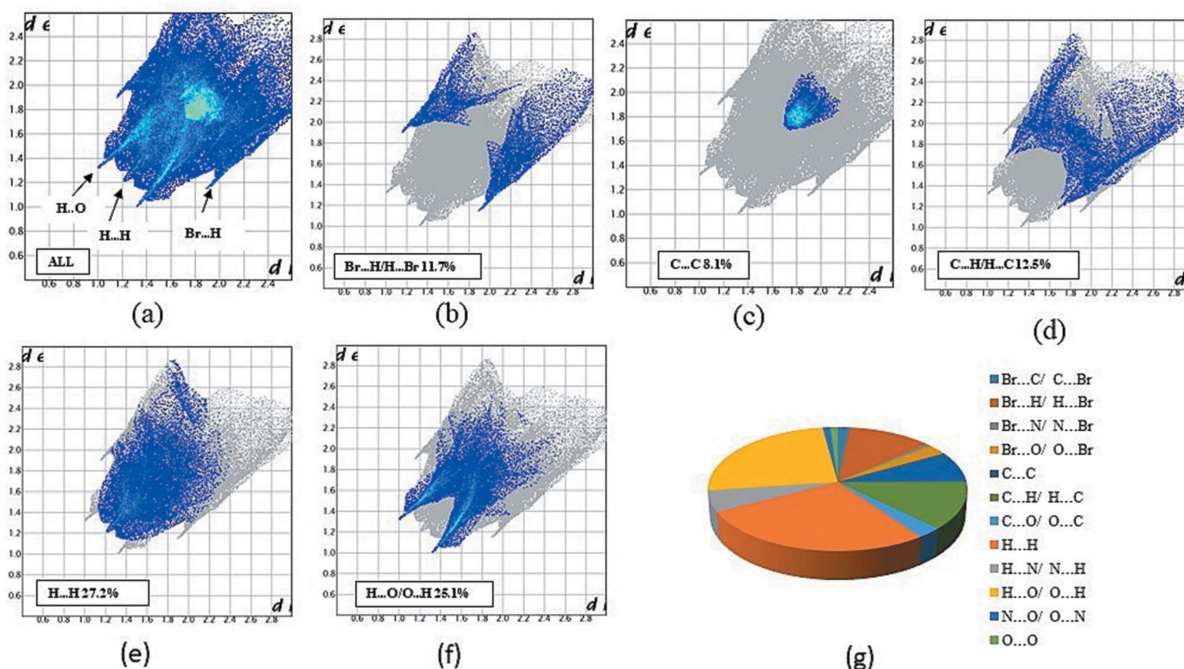
and slippage = 1.115 Å], which also contributes to the molecular packing. The Br atom does not take part in any interactions. The nearest Br...C7($-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$) distance in the molecular structure is 3.6112 (7) Å.

Hirshfeld surface analysis serves as a powerful tool for gaining additional insight into intermolecular interactions of molecular crystals. The Hirshfeld surfaces are mapped with 2D fingerprint plots presented using *CrystalExplorer3.1* and it provides a summary of the intermolecular contacts in the crystal (McKinnon *et al.*, 2004; Spackman & Jayatilaka, 2009). The 2D fingerprint plots (Fig. 3) show that the intermolecular H...H and O...H interactions dominate and complement the Hirshfeld surfaces. The fingerprint plots can also be decomposed to highlight particular atom-pair close contacts (Luo *et al.*, 2013) and enables separation of contributions from different interaction types. Two sharp spikes pointing towards the upper left of the plot are typical C—H...O hydrogen

bonds. This portion corresponds to H...O interactions comprising 25.1% of the total Hirshfeld surfaces. Two sharp spikes pointing towards the lower left of the plot are typical Br...H hydrogen bonds. This portion corresponds to Br...H interactions comprising 11.7% of the total Hirshfeld surfaces. The broad region bearing short and narrow spikes at the middle of plot is reflected as H...H interaction comprising 27.2% of the total Hirshfeld surfaces. Apart from these, the presence of Br...C, Br...N, Br...O, C...O, H...N, N...O and O...O interactions were observed (Pi chart; Fig. 4g), which are summarized in Table 2 (Li *et al.*, 2013; Luo & Sun, 2014; Seth *et al.*, 2011).

4. Database survey

While searching for 2-phenylhydrazine in the Cambridge Structural Database (CSD, Version 53.7; Groom *et al.*, 2016), four significant structures were found [CSD refcodes AYSOD (Tahir *et al.*, 2011), DUSBID (Mufakkar *et al.* 2010), DUSNUB (Shad *et al.* 2010) and DUSNUB01 (Toledano-Magaña *et al.*, 2015)]. Also, the crystal structure of the unsubstituted phenyl hydrazine has been reported in the CSD [ZZZGWW02 (Vickery *et al.*, 1985) and ZZZGWW03 (Günes, *et al.*, 2003)]. The two phenyl rings in AYSOD (two molecules in the asymmetric unit), DUSBID and DUSNUB (two molecules in the asymmetric unit) are inclined to each other by 2.44 (18) and 14.08 (19)° (in molecules *A* and *B*), 9.30 (6)°, and 13.01 (10) and 14.05 (10)° (in molecules *A* and *B*), respectively, compared to 4.4 (3)° in the title compound. The crystal packing of the two compounds is significantly different. In AYSOD, N—H groups do not form hydrogen bonds, in DUSBID, the molecules are linked by N—H... π interactions,


Figure 3

The full two-dimensional fingerprint plots, and those delineated into (a) all interactions (b) Br...H, (c) C...C, (d) C...H/H...C, (e) H...H and (f) H...O/O...H contacts showing the percentages of contacts contributed to the total Hirshfeld surface area. (g) Pi chart.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₆ H ₁₄ BrN ₃ O ₅
<i>M_r</i>	408.21
Crystal system, space group	Monoclinic, <i>P2₁/n</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3262 (11), 14.8369 (19), 14.0764 (13)
β (°)	106.558 (14)
<i>V</i> (Å ³)	1666.8 (4)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	2.50
Crystal size (mm)	0.09 × 0.08 × 0.06
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (North <i>et al.</i> , 1968)
<i>T_{min}</i> , <i>T_{max}</i>	0.666, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4830, 3187, 1726
<i>R_{int}</i>	0.065
(sin θ/λ) _{max} (Å ⁻¹)	0.682
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.096, 0.202, 1.09
No. of reflections	3187
No. of parameters	235
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.66, -0.69

Computer programs: APEX2 and SAINT (Bruker, 2008), SHELXS97 and SHELXL97 (Sheldrick, 2008) and PLATON (Spek, 2009).

and in DUSNUB, both molecules form inversion dimers linked by pairs of N—H···O hydrogen bonds, thereby generating *R*₂²(16) motif rings (Bernstein *et al.*, 1995). In the title compound, intramolecular N—H···O and only intermolecular C—H···O hydrogen bonds are present; there are no C—H···π interactions. Very few similar hydrazine derivatives are reported in the literature (Cortés *et al.*, 2013; Dey & Chopra, 2017). In those crystal structures, a halogen group (Cl and F, respectively) is present, while in this crystal structure, Br is present.

5. Synthesis and crystallization

The title compound was synthesized in one step by heating the hydrazine derivative 3-nitrobenzohydrazide (0.181 mg) with a slight excess of 5-bromo-2-methoxybenzaldehyde (0.215 mg) in an acetic acid solution (10 ml). The reaction mixture was refluxed for 8 h. The solid product formed during reflux was filtered off, washed and dried over anhydrous calcium chloride in a vacuum desiccator (yield 75%). The final product was soluble in acetone, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), methanol, ethanol and ethyl acetate, *etc.* Transparent orange-coloured needle-shaped diffraction-quality single crystals of the title compound were grown by slow evaporation using methanol as the solvent at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The coordinates of the H atoms of the N2—H2 and C9—H9 groups were refined [N2—H2 = 0.83 (6) Å and C9—H9 = 0.90 (5) Å]. Other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93–0.97 Å, and refined as riding with *U*_{iso}(H) = *xU*_{eq}(C), where *x* = 1.5 for methyl and *x* = 1.2 for all other H atoms.

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References

- Banerjee, S., Mondal, S., Chakraborty, W., Sen, S., Gachhui, R., Butcher, R. J., Slawin, A. M. Z., Mandal, C. & Mitra, S. (2009). *Polyhedron*, **28**, 2785–2793.
- Belskaya, N. P., Dehaen, W. & Bakulev, V. A. (2010). *Arch. Org. Chem.* **1**, 275–332.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bruker (2008). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Corey, E. J. & Enders, D. (1976). *Tetrahedron Lett.* **17**, 11–14.
- Cortés, E., Abonía, R., Cobo, J. & Glidewell, C. (2013). *Acta Cryst.* **C69**, 754–760.
- Dey, D. & Chopra, D. (2017). *Acta Cryst.* **B73**, 781–793.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Günes, B., Özbey, S. & Tezcan, H. (2003). *Anal. Sci.* **19**, 1091–1092.
- Levrant, B., Fiebera, W., Lehn, J.-M. & Herrmann, A. (2007). *Helv. Chim. Acta*, **90**, 2281–2314.
- Li, Y., Zhang, C. G., Cai, L. Y. & Wang, Z. X. (2013). *J. Coord. Chem.* **66**, 3100–3112.
- Li, L., Zhu, L., Chen, D., Hu, X. & Wang, R. (2011). *Eur. J. Org. Chem.* pp. 2692–2696.
- Luo, Y. H. & Sun, B. W. (2014). *Spectrochim. Acta Part A*, **120**, 381–388.
- Luo, Y. H., Wu, G. G., Mao, S. L. & Sun, B. W. (2013). *Inorg. Chim. Acta*, **397**, 1–9.
- McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Cryst.* **B60**, 627–668.
- Mufakkar, M., Tahir, M. N., Tariq, M. I., Ahmad, S. & Sarfraz, M. (2010). *Acta Cryst.* **E66**, o1887.
- Narang, R., Narasimhan, B. & Sharma, S. (2012). *Curr. Med. Chem.* **19**, 569–612.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rollas, S. & Küçükgül, S. G. (2007). *Molecules*, **12**, 1910–1939.
- Seth, S. K., Mandal, P. C., Kar, T. & Mukhopadhyay, S. (2011). *J. Mol. Struct.* **994**, 109–116.
- Shad, H. A., Tahir, M. N., Tariq, M. I., Sarfraz, M. & Ahmad, S. (2010). *Acta Cryst.* **E66**, o1955.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tahir, M. N., Tariq, M. I., Tariq, R. H. & Sarfraz, M. (2011). *Acta Cryst.* **E67**, o2377.

- Toledano-Magaña, Y., García-Ramos, J. C., Navarro-Olivarria, M., Flores-Alamo, M., Manzanera-Estrada, M., Ortiz-Frade, L., Galindo-Murillo, R., Ruiz-Azuara, L., Meléndrez-Luevano, R. M. & Cabrera-Vivas, B. M. (2015). *Molecules*, **20**, 9929–9948.
- Uppal, G., Bala, S., Kamboj, S. & Saini, M. (2011). *Der. Pharma Chem.* **3**, 250–68.
- Vickery, B., Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* **C41**, 1072–1075.
- Wu, A., Senter, M. & Peter, D. (2005). *Nat. Biotechnol.* **23**, 1137–1146.
- Xavier, A. J., Thakur, M. & Marie, J. M. (2012). *J. Chem. Pharm. Res.* **4**, 986–990.

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Methyl 4-[(*E*)-2-(5-bromo-2-methoxybenzylidene)hydrazinyl]-3-nitrobenzoate

Crystal data

C₁₆H₁₄BrN₃O₅

M_r = 408.21

Monoclinic, *P2₁/n*

a = 8.3262 (11) Å

b = 14.8369 (19) Å

c = 14.0764 (13) Å

β = 106.558 (14)°

V = 1666.8 (4) Å³

Z = 4

F(000) = 824

D_x = 1.627 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 1261 reflections

θ = 3.3–23.2°

μ = 2.50 mm⁻¹

T = 293 K

Plate, yellow

0.09 × 0.08 × 0.06 mm

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan

(North *et al.*, 1968)

T_{min} = 0.666, *T_{max}* = 1.000

4830 measured reflections

3187 independent reflections

1726 reflections with *I* > 2σ(*I*)

R_{int} = 0.065

θ_{max} = 29.0°, θ_{min} = 3.6°

h = -10→11

k = -19→10

l = -9→18

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.096

wR(*F*²) = 0.202

S = 1.09

3187 reflections

235 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0381*P*)² + 5.1653*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.66 e Å⁻³

Δρ_{min} = -0.69 e Å⁻³

Extinction correction: SHELXL97 (Sheldrick,
2008), *F_c** = *kF_c*[1 + 0.001*xF_c*²λ³/sin(2θ)]^{-1/4}

Extinction coefficient: 0.0076 (10)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3935 (9)	0.2162 (5)	0.6270 (5)	0.038 (2)
H1	0.415174	0.223200	0.695123	0.046*
C2	0.2457 (9)	0.1749 (5)	0.5739 (5)	0.0348 (19)
C3	0.2169 (9)	0.1645 (5)	0.4728 (5)	0.0339 (18)
H3	0.118584	0.137270	0.435409	0.041*
C4	0.3340 (9)	0.1944 (5)	0.4272 (5)	0.0328 (18)
C5	0.4810 (9)	0.2391 (5)	0.4784 (5)	0.0308 (17)
C6	0.5083 (9)	0.2468 (6)	0.5818 (5)	0.040 (2)
H6	0.606744	0.273342	0.620051	0.049*
C7	0.1197 (10)	0.1486 (6)	0.6245 (6)	0.0386 (19)
C8	-0.1484 (10)	0.0834 (7)	0.6023 (6)	0.061 (3)
H8A	-0.236862	0.055874	0.551367	0.091*
H8B	-0.107222	0.041302	0.655468	0.091*
H8C	-0.190635	0.135968	0.626904	0.091*
C9	0.8528 (10)	0.3310 (6)	0.4527 (5)	0.040 (2)
C10	1.0108 (9)	0.3711 (6)	0.5111 (5)	0.0373 (19)
C11	1.1267 (10)	0.4052 (5)	0.4648 (6)	0.040 (2)
C12	1.2709 (10)	0.4470 (6)	0.5203 (6)	0.046 (2)
H12	1.345065	0.471252	0.488742	0.055*
C13	1.3069 (10)	0.4532 (6)	0.6226 (6)	0.052 (2)
H13	1.404718	0.480982	0.659877	0.063*
C14	1.1940 (10)	0.4174 (6)	0.6681 (5)	0.043 (2)
C15	1.0485 (9)	0.3762 (5)	0.6140 (5)	0.0357 (18)
H15	0.975310	0.351682	0.646202	0.043*
C16	1.1856 (12)	0.4401 (7)	0.3120 (6)	0.069 (3)
H16A	1.141419	0.428322	0.242387	0.104*
H16B	1.185656	0.503869	0.323555	0.104*
H16C	1.298062	0.417511	0.335016	0.104*
N1	0.2911 (8)	0.1797 (5)	0.3208 (4)	0.0370 (16)
N2	0.5978 (8)	0.2714 (5)	0.4364 (5)	0.0424 (18)
N3	0.7457 (8)	0.3049 (5)	0.4962 (4)	0.0393 (16)
O1	-0.0146 (7)	0.1088 (4)	0.5621 (4)	0.0494 (16)
O2	0.1325 (7)	0.1613 (4)	0.7107 (4)	0.0548 (17)
O3	0.1809 (8)	0.1260 (5)	0.2817 (4)	0.0612 (18)
O4	0.3693 (6)	0.2228 (4)	0.2728 (3)	0.0544 (17)
O5	1.0838 (7)	0.3963 (4)	0.3644 (4)	0.0545 (17)
BR1	1.24638 (13)	0.41918 (8)	0.80847 (6)	0.0681 (5)
H2A	0.576 (7)	0.270 (4)	0.375 (4)	0.014 (16)*
H9	0.825 (7)	0.329 (4)	0.386 (4)	0.012 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.037 (4)	0.050 (6)	0.025 (3)	0.001 (4)	0.004 (4)	0.002 (4)
C2	0.035 (4)	0.046 (5)	0.025 (3)	0.004 (4)	0.011 (3)	0.004 (3)
C3	0.033 (4)	0.040 (5)	0.028 (3)	0.005 (4)	0.007 (3)	0.004 (3)
C4	0.038 (4)	0.040 (5)	0.020 (3)	0.002 (4)	0.008 (3)	−0.003 (3)
C5	0.025 (4)	0.039 (5)	0.028 (3)	0.001 (4)	0.006 (3)	−0.003 (3)
C6	0.033 (4)	0.056 (6)	0.030 (3)	−0.003 (4)	0.006 (4)	−0.005 (4)
C7	0.038 (4)	0.041 (6)	0.039 (4)	0.008 (4)	0.016 (4)	0.004 (4)
C8	0.038 (5)	0.091 (8)	0.059 (5)	−0.003 (5)	0.022 (4)	0.007 (5)
C9	0.037 (5)	0.051 (6)	0.027 (4)	0.002 (4)	0.004 (4)	−0.001 (4)
C10	0.032 (4)	0.044 (5)	0.035 (4)	0.007 (4)	0.008 (4)	0.003 (4)
C11	0.035 (4)	0.040 (6)	0.042 (4)	0.006 (4)	0.010 (4)	0.004 (4)
C12	0.039 (5)	0.042 (6)	0.056 (5)	−0.008 (4)	0.012 (4)	−0.001 (4)
C13	0.039 (5)	0.055 (6)	0.060 (5)	0.000 (4)	0.011 (5)	0.003 (5)
C14	0.044 (5)	0.042 (6)	0.037 (4)	0.003 (4)	0.002 (4)	−0.001 (4)
C15	0.031 (4)	0.037 (5)	0.038 (4)	−0.006 (4)	0.007 (4)	−0.003 (4)
C16	0.073 (6)	0.095 (9)	0.052 (5)	−0.006 (6)	0.037 (5)	0.010 (5)
N1	0.034 (4)	0.053 (5)	0.025 (3)	0.001 (3)	0.011 (3)	0.003 (3)
N2	0.038 (4)	0.064 (5)	0.025 (3)	−0.002 (4)	0.008 (3)	−0.004 (3)
N3	0.033 (4)	0.053 (5)	0.030 (3)	−0.009 (3)	0.004 (3)	−0.003 (3)
O1	0.044 (3)	0.070 (5)	0.040 (3)	−0.005 (3)	0.021 (3)	0.000 (3)
O2	0.060 (4)	0.079 (5)	0.031 (3)	0.002 (3)	0.023 (3)	0.000 (3)
O3	0.065 (4)	0.081 (5)	0.032 (3)	−0.035 (4)	0.004 (3)	−0.012 (3)
O4	0.046 (3)	0.090 (5)	0.028 (3)	−0.012 (3)	0.013 (3)	−0.001 (3)
O5	0.054 (4)	0.075 (5)	0.038 (3)	−0.008 (3)	0.020 (3)	0.005 (3)
BR1	0.0721 (8)	0.0855 (9)	0.0375 (5)	−0.0200 (6)	0.0007 (5)	−0.0053 (5)

Geometric parameters (Å, °)

C1—C6	1.369 (10)	C9—H9	0.90 (5)
C1—C2	1.386 (10)	C10—C15	1.394 (9)
C1—H1	0.9300	C10—C11	1.404 (10)
C2—C3	1.383 (9)	C11—O5	1.362 (9)
C2—C7	1.479 (10)	C11—C12	1.379 (11)
C3—C4	1.385 (9)	C12—C13	1.388 (11)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.399 (10)	C13—C14	1.385 (11)
C4—N1	1.454 (8)	C13—H13	0.9300
C5—N2	1.361 (9)	C14—C15	1.377 (10)
C5—C6	1.411 (9)	C14—BR1	1.899 (7)
C6—H6	0.9300	C15—H15	0.9300
C7—O2	1.201 (8)	C16—O5	1.428 (9)
C7—O1	1.346 (9)	C16—H16A	0.9600
C8—O1	1.437 (9)	C16—H16B	0.9600
C8—H8A	0.9600	C16—H16C	0.9600
C8—H8B	0.9600	N1—O3	1.221 (8)

C8—H8C	0.9600	N1—O4	1.240 (7)
C9—N3	1.277 (9)	N2—N3	1.371 (8)
C9—C10	1.464 (11)	N2—H2A	0.83 (6)
C6—C1—C2	121.8 (6)	C11—C10—C9	120.8 (7)
C6—C1—H1	119.1	O5—C11—C12	124.1 (7)
C2—C1—H1	119.1	O5—C11—C10	115.8 (7)
C3—C2—C1	118.1 (7)	C12—C11—C10	120.1 (7)
C3—C2—C7	121.8 (7)	C11—C12—C13	120.9 (8)
C1—C2—C7	120.0 (6)	C11—C12—H12	119.5
C2—C3—C4	120.2 (7)	C13—C12—H12	119.5
C2—C3—H3	119.9	C14—C13—C12	118.6 (8)
C4—C3—H3	119.9	C14—C13—H13	120.7
C3—C4—C5	122.8 (6)	C12—C13—H13	120.7
C3—C4—N1	115.5 (7)	C15—C14—C13	121.5 (7)
C5—C4—N1	121.7 (6)	C15—C14—BR1	119.1 (6)
N2—C5—C4	124.8 (6)	C13—C14—BR1	119.4 (6)
N2—C5—C6	119.6 (7)	C14—C15—C10	120.0 (7)
C4—C5—C6	115.5 (6)	C14—C15—H15	120.0
C1—C6—C5	121.6 (7)	C10—C15—H15	120.0
C1—C6—H6	119.2	O5—C16—H16A	109.5
C5—C6—H6	119.2	O5—C16—H16B	109.5
O2—C7—O1	123.1 (7)	H16A—C16—H16B	109.5
O2—C7—C2	125.0 (8)	O5—C16—H16C	109.5
O1—C7—C2	111.9 (6)	H16A—C16—H16C	109.5
O1—C8—H8A	109.5	H16B—C16—H16C	109.5
O1—C8—H8B	109.5	O3—N1—O4	122.3 (6)
H8A—C8—H8B	109.5	O3—N1—C4	119.6 (6)
O1—C8—H8C	109.5	O4—N1—C4	118.0 (6)
H8A—C8—H8C	109.5	C5—N2—N3	119.2 (6)
H8B—C8—H8C	109.5	C5—N2—H2A	118 (4)
N3—C9—C10	119.5 (7)	N3—N2—H2A	122 (4)
N3—C9—H9	119 (4)	C9—N3—N2	116.3 (6)
C10—C9—H9	121 (4)	C7—O1—C8	116.8 (6)
C15—C10—C11	118.9 (7)	C11—O5—C16	118.2 (7)
C15—C10—C9	120.3 (7)		

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>
N2—H2A...O4	0.83	2.03	2.635 (3)	129
C3—H3...O1	0.93	2.39	2.712 (4)	100
C6—H6...N3	0.93	2.40	2.731 (4)	101
C6—H6...O4 ⁱ	0.93	2.59	3.444 (5)	152
C15—H15...O4 ⁱ	0.93	2.46	3.358 (4)	161

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