



# (*E*)-3-[[2-(2-Bromo-3-methylphenyl)imino]methyl]benzene-1,2-diol: crystal structure and Hirshfeld surface analysis

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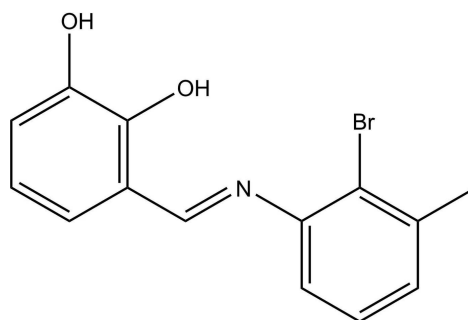
**Keywords:** crystal structure; Schiff base; O...O interaction; Hirshfeld surface analysis; hydrogen bonds.**CCDC reference:** 1967023**Supporting information:** this article has supporting information at journals.iucr.org/e

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The title compound, C<sub>14</sub>H<sub>12</sub>BrNO<sub>2</sub>, was synthesized by the condensation reaction of 2,3-dihydroxybenzaldehyde and 2-bromo-3-methylaniline. It crystallizes in the centrosymmetric triclinic space group *P* $\bar{1}$ . The configuration about the C=N bond is *E*. The dihedral angle between the planes of the 5-(2-bromo-3-methylphenyl) ring and the catechol ring is 2.80 (17)°. In the crystal, O—H...O hydrogen-bond interactions consolidate the crystal packing.

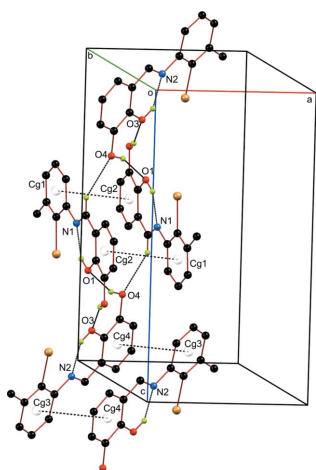
## 1. Chemical context

Schiff bases containing an azomethine or imine (—C=N—) unit are condensation products of primary amines and carbonyl compounds that were first reported by Hugo Schiff (1864). Schiff bases have a wide variety of applications in many areas of biological, organic and inorganic chemistry. The medicinal uses and applications of Schiff bases and their metal complexes are of increasing clinical and commercial importance and are increasingly significant in the medicinal and pharmaceutical fields because of their extensive range of biological activities (Karthikeyan *et al.*, 2006).



## 2. Structural commentary

The structure of the title compound is shown in Fig. 1. It crystallizes in the centrosymmetric *P* $\bar{1}$  space group with *Z* = 4 (*Z*' = 2). The two crystallographically independent molecules have nearly the same geometrical parameters and the primary difference between them is the rotational orientation of H2 and H4A. The discussion will therefore be limited to that of the molecule containing O1. The molecular structure is constructed from two individually planar rings. The whole molecule is approximately planar, with a maximum deviation of 0.117 (3) Å from planarity for the hydroxyl O1 atom of the



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

| $D-H\cdots A$                  | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|-------|-------------|-------------|---------------|
| O1–H1 $\cdots$ N1              | 0.82  | 1.85        | 2.571 (3)   | 146           |
| O3–H3 $\cdots$ N2              | 0.82  | 1.85        | 2.560 (3)   | 145           |
| O4–H4A $\cdots$ O1             | 0.82  | 2.02        | 2.790 (4)   | 157           |
| O2–H2 $\cdots$ O3              | 0.82  | 2.11        | 2.875 (3)   | 156           |
| C8–H8 $\cdots$ O4 <sup>i</sup> | 0.93  | 2.54        | 3.383 (4)   | 151           |

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

catechol ring. The dihedral angle between the two benzene ring planes is  $2.80 (17)^\circ$ . The methyl C1 atom deviates from the plane of the C2–C7 benzene ring by  $0.039 (2)$  Å while C9 deviates from the plane of the C9–C14 benzene ring by  $0.024 (3)$  Å. The C8–N1–C7–C6 and C14–C9–C8–N1 torsion angles are  $-1.6 (5)$  and  $-1.1 (5)^\circ$ , respectively. The planar molecular conformation of each molecule is stabilized by an intramolecular O–H $\cdots$ N hydrogen bond (Table 1).

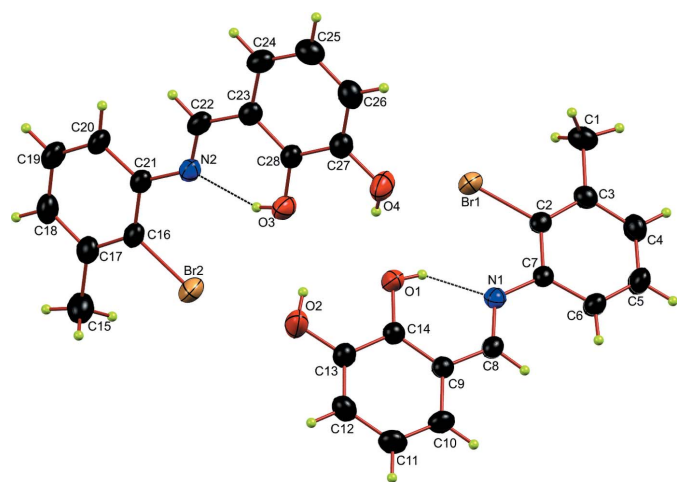
### 3. Supramolecular features

In the crystal, the Schiff base units are linked by O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonds (O4–H4A $\cdots$ O1, O2–H2 $\cdots$ O3 and C8–H8 $\cdots$ O4<sup>i</sup>; symmetry code as in Table 1), forming a tape structure along the  $a$ -axis direction (Fig. 2). The tapes are stacked into layers parallel to the benzene plane *via*  $\pi$ – $\pi$  interactions (Fig. 2) with centroid–centroid distances of  $3.750 (2)$  and  $3.783 (2)$  Å, respectively, for Cg1 $\cdots$ Cg2( $1 - x, 1 - y, 1 - z$ ) and Cg3 $\cdots$ Cg4( $-x, 1 - y, -z$ ), where Cg1, Cg2, Cg3 and Cg4 are the centroids of the C2–C7, C9–C14, C16–C21 and C23–C28 rings, respectively.

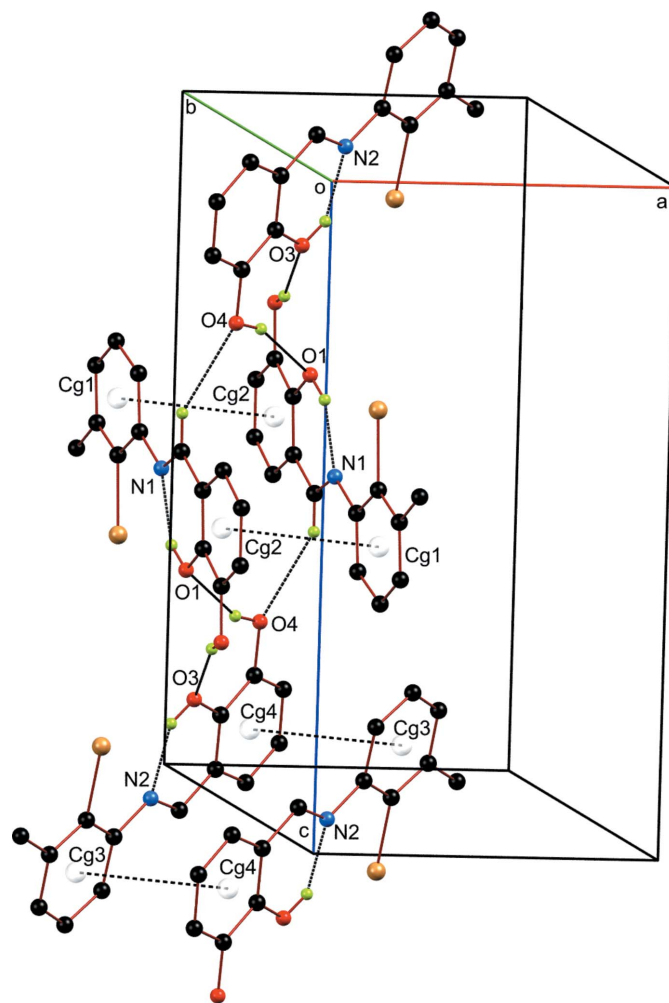
### 4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40, update Nov 2018; Groom *et al.*, 2016) for the (*E*)-*N*-(2-

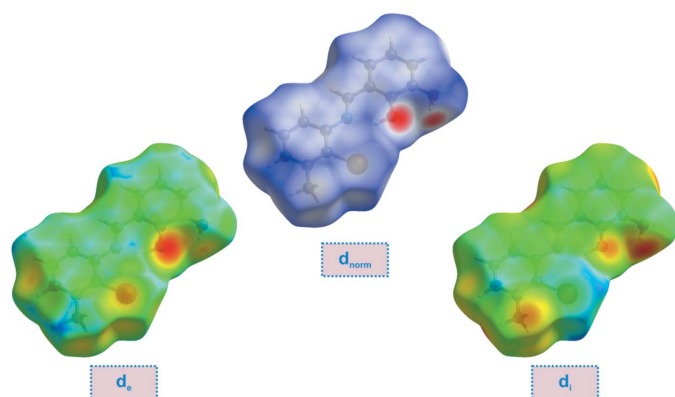
bromophenyl)-1-phenylmethanimine skeleton yielded nine hits. The N1–C8 bond in the title structure is the same length within standard uncertainties as those in the structures of 2-bromo-*N*-salicylideneaniline (Burr & Hobson, 1969), *N*-(2-bromophenyl)-1-(2-fluorophenyl)methanimine (Kaur & Choudhury, 2014), 2-[(*E*)-(2,4-dibromophenylimino)methyl]-4-bromophenol (Bharti *et al.*, 2017), *N*-(2-bromo-4-methylphenyl)naphthalidimine (Elmali *et al.*, 1998), *N*-(2-methylbenzylidene)-2-bromoaniline (Ojala *et al.*, 2007), 2-[[2-(2-bromophenyl)imino]methyl]-4-chlorophenol (Guo, 2011), 2-[[2-(2-bromophenyl)imino]methyl]-4-chlorophenol (Zhao & Zhang, 2012), 2-[[2-(2-bromophenyl)imino]methyl]-6-methylphenol (Karadağ *et al.*, 2010), 2-[[2-(2-bromophenyl)imino]methyl]-4-(trifluoromethoxy)phenol (Tanak *et al.*, 2012). The C=N bond lengths in these structures vary from  $1.270 (3)$  to  $1.295 (5)$  Å and the C–O bond lengths from  $1.336 (5)$  to  $1.366 (2)$  Å. The molecular conformations of these structures are also not planar, with dihedral angles between the phenyl rings varying between  $5.00 (5)$  and  $47.62 (9)^\circ$ . It is likely that the intramolecular O–H $\cdots$ N hydrogen bond, where the



**Figure 1**  
The molecular structure of the title compound with the atomic numbering scheme. The dashed lines indicate the intramolecular O–H $\cdots$ N hydrogen bonds. Displacement ellipsoids are drawn at the 30% probability level.

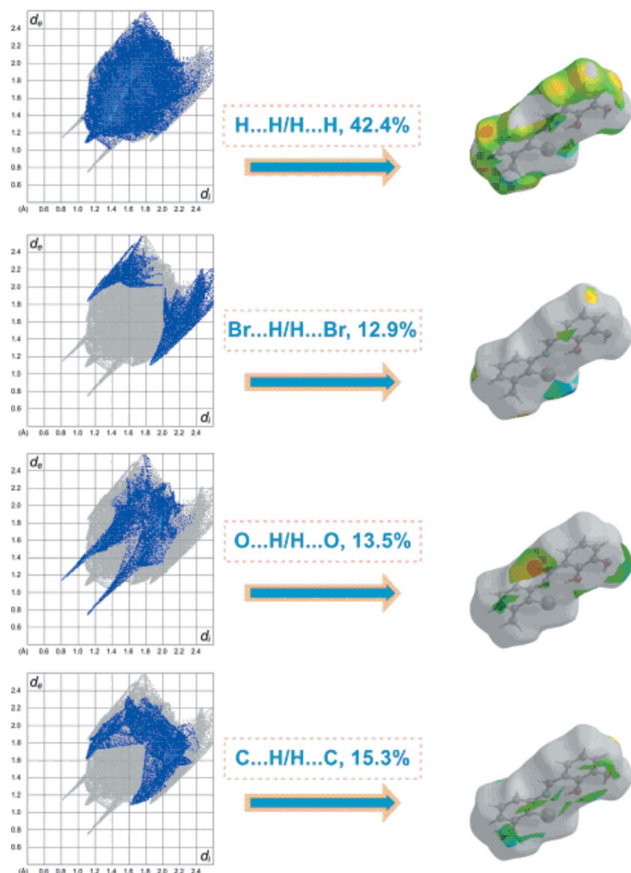


**Figure 2**  
A partial view of the crystal packing of the title compound. Intra- and intermolecular hydrogen bonds are shown as dotted lines while the  $\pi$ -stacking interactions are depicted by dashed lines.

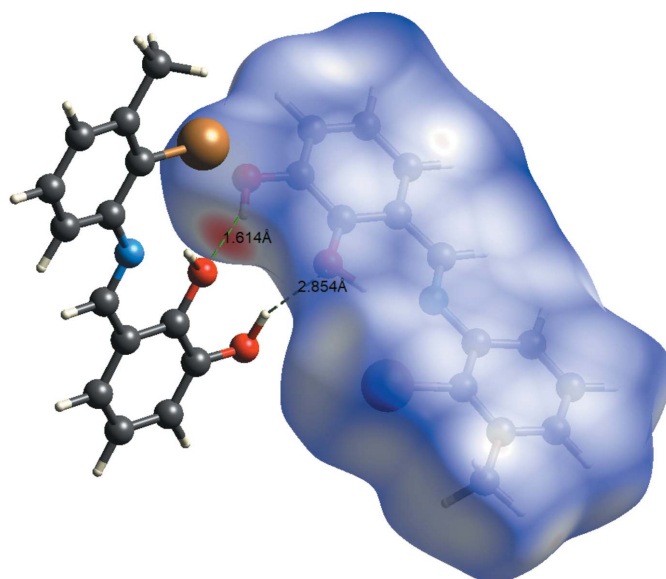


**Figure 3**  
View of the three-dimensional Hirshfeld surface of the title compound plotted over  $d_{\text{norm}}$ ,  $d_e$  and  $d_i$ .

imine N atom acts as an hydrogen-bond acceptor, is an important prerequisite for the tautomeric shift toward the phenol–imine form. In fact, in all eight structures of the phenol–imine tautomers, hydrogen bonds of this type are observed.



**Figure 4**  
Two-dimensional fingerprint plots of the crystal with the relative contributions of the atom pairs to the Hirshfeld surface.



**Figure 5**  
Hirshfeld surface mapped over  $d_{\text{norm}}$  to visualize the intermolecular interactions.

## 5. Hirshfeld surface analysis

Hirshfeld surface analysis of the title compound was performed utilizing the *CrystalExplorer* program (Turner *et al.*, 2017). The three-dimensional  $d_{\text{norm}}$  surface is a useful tool for analysing and visualizing the intermolecular interactions and utilizes the function of the normalized distances  $d_e$  and  $d_i$ , where  $d_e$  and  $d_i$  are the distances from a given point on the surface to the nearest atom outside and inside, respectively. The blue, white and red colour convention used for the  $d_{\text{norm}}$ -mapped Hirshfeld surfaces indicates the interatomic contacts longer, equal to or shorter than the van der Waals separations. The standard-resolution molecular three-dimensional ( $d_{\text{norm}}$ ) plot with  $d_e$  and  $d_i$  for the title compound is shown in Fig. 3. The bright-red spots near the oxygen and hydrogen atoms indicate donors and acceptors of a potential O–H...O interaction. As can be seen from the two-dimensional fingerprint plots (scattering points spread up to  $d_e = d_i = 1.5$  Å; Fig. 4), the dominant interaction in the title compound originates from H...H contacts, which are the major contributor (42.4%) to the total Hirshfeld surface. The contribution from the O...H/H...O contacts (13.5%) is represented by a pair of sharp spikes that are characteristic of hydrogen-bonding interactions (Fig. 4). Other significant interactions are Br...H/H...Br (12.9%) and C...H/H...C (15.3%). While it is likely there are other identifiable points of contact that can be highlighted in the crystal, these may be of limited significance and do not require detailed discussion nor illustration. The interactions are visualized in Fig. 5.

## 6. Synthesis and crystallization

A mixture of 2,3-dihydroxybenzaldehyde (34.5 mg, 0.25 mmol) and 2-bromo-3-methylaniline (46.5 mg, 0.25 mmol) was stirred with ethanol (30 mL) at 377 K for 5 h,

**Table 2**  
Experimental details.

|   |   |
|---|---|
| Crystal data  |   |
| Chemical formula  | C <sub>14</sub> H <sub>12</sub> BrNO <sub>2</sub> |
| <i>M</i> <sub>r</sub>   | 306.16  |
| Crystal system, space group   | Triclinic, <i>P</i> $\bar{1}$                     |
| Temperature (K)   | 296   |
| <i>a</i> , <i>b</i> , <i>c</i> (Å)  | 8.2301 (5), 10.1593 (6), 15.9428 (9)              |
| $\alpha$ , $\beta$ , $\gamma$ (°)   | 102.496 (5), 90.597 (5), 103.213 (5)              |
| <i>V</i> (Å <sup>3</sup> )  | 1264.46 (13)                                      |
| <i>Z</i>  | 4   |
| Radiation type  | Mo <i>K</i> $\alpha$                              |
| $\mu$ (mm <sup>-1</sup> )   | 3.24  |
| Crystal size (mm)   | 0.49 × 0.31 × 0.21                                |
| Data collection   |   |
| Diffractometer  | Stoe <i>IPDS</i> 2                                |
| Absorption correction   | Integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)  |
| <i>T</i> <sub>min</sub> – <i>T</i> <sub>max</sub>   | 0.441, 0.663                                      |
| No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections                             | 13105, 4958, 3352                                 |
| <i>R</i> <sub>int</sub>   | 0.044   |
| (sin $\theta$ / $\lambda$ ) <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> | 0.038, 0.081, 0.97                                |
| No. of reflections  | 4958  |
| No. of parameters   | 331   |
| H-atom treatment  | H-atom parameters constrained                     |
| $\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )  | 0.38, -0.26                                       |

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2009).

affording the title compound (49.73 mg, yield 65% m.p. 410–412 K). Single crystals suitable for X-ray measurements were obtained by recrystallization from ethanol at room temperature.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxy H atom was located in a difference-Fourier map, and the hydroxy group was allowed to rotate during the refinement procedure (AFIX 147); O–H = 0.82 Å with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O). The C-bound

H atoms were positioned geometrically and refined using a riding model: C–H = 0.93 Å with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) for aromatic H atoms and C–H = 0.96 Å with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for methyl H atoms.

## Acknowledgements

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## References

- Bharti, S., Choudhary, M., Mohan, B., Rawat, S., Sharma, S. & Ahmad, K. (2017). *J. Mol. Struct.* **1149**, 846–861.
- Burr, A. H. & Hobson, A. D. (1969). *Acta Cryst.* **B25**, 2662–2663.
- Elmali, A., Elerman, Y. & Kendi, E. (1998). *Acta Cryst.* **C54**, 1137–1139.
- 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.
- Guo, Y.-N. (2011). *Wuji Huaxue Xuebao*, **27**, 1875–1880.
- Karadağ, A. T., Atalay, Ş. & Genç, H. (2010). *Acta Cryst.* **E66**, o2977.
- Karthikeyan, M. S., Prasad, D. J., Poojary, B., Bhat, K. S., Holla, B. S. & Kumari, N. S. (2006). *Bioorg. Med. Chem.* **14**, 7482–7489.
- Kaur, G. & Choudhury, A. R. (2014). *Cryst. Growth Des.* **14**, 1600–1616.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Ojala, W. H., Smieja, J. M., Spude, J. M., Arola, T. M., Kuspa, M. K., Herrera, N. & Ojala, C. R. (2007). *Acta Cryst.* **B63**, 485–496.
- Schiff, H. (1864). *Ann. Chem. Pharm.* **131**, 118–119.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie GmbH, Darmstadt, Germany.
- Tanak, H., Açar, A. A. & Büyükgüngör, O. (2012). *Spectrochim. Acta Part A*, **87**, 15–24.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia.
- Zhao, F.-W. & Zhang, F. (2012). *Z. Kristallogr. New Cryst. Struct.* **227**, 53–54.

## supporting information

*Acta Cryst.* (2019). E75, 1930-1933 [https://doi.org/10.1107/S2056989019015718]

## (*E*)-3-[(2-Bromo-3-methylphenyl)imino]methyl}benzene-1,2-diol: crystal structure and Hirshfeld surface analysis

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### Computing details

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *WinGX* (Farrugia, 2012); program(s) used to refine structure: *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *Mercury* (Macrae *et al.*, 2006), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

### (*E*)-3-[(2-Bromo-3-methylphenyl)imino]methyl}benzene-1,2-diol

#### Crystal data

C<sub>14</sub>H<sub>12</sub>BrNO<sub>2</sub>

$M_r = 306.16$

Triclinic, *P* $\bar{1}$

$a = 8.2301$  (5) Å

$b = 10.1593$  (6) Å

$c = 15.9428$  (9) Å

$\alpha = 102.496$  (5)°

$\beta = 90.597$  (5)°

$\gamma = 103.213$  (5)°

$V = 1264.46$  (13) Å<sup>3</sup>

$Z = 4$

$F(000) = 616$

$D_x = 1.608$  Mg m<sup>-3</sup>

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

Cell parameters from 15203 reflections

$\theta = 2.1$ – $32.4$ °

$\mu = 3.24$  mm<sup>-1</sup>

$T = 296$  K

Column, red

$0.49 \times 0.31 \times 0.21$  mm

#### Data collection

Stoe IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4

mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm<sup>-1</sup>

rotation method scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\min} = 0.441$ ,  $T_{\max} = 0.663$

13105 measured reflections

4958 independent reflections

3352 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 26.0$ °,  $\theta_{\min} = 2.1$ °

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -19 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.081$

$S = 0.97$

4958 reflections

331 parameters

0 restraints

Primary atom site location: intrinsic phasing

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2]$

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

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

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

### 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            | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| Br1 | 0.47553 (5) | 0.73422 (3) | 0.43378 (2)  | 0.06496 (13)                     |
| Br2 | 0.27549 (6) | 0.20843 (4) | 0.05124 (2)  | 0.07628 (15)                     |
| O1  | 0.1481 (3)  | 0.4451 (2)  | 0.34610 (15) | 0.0653 (7)                       |
| H1  | 0.211056    | 0.487560    | 0.388310     | 0.098*                           |
| O3  | 0.1364 (4)  | 0.4958 (2)  | 0.16060 (16) | 0.0691 (7)                       |
| H3  | 0.189385    | 0.466512    | 0.120398     | 0.104*                           |
| N1  | 0.2564 (3)  | 0.5099 (2)  | 0.50502 (16) | 0.0470 (6)                       |
| N2  | 0.2469 (3)  | 0.4778 (3)  | 0.01003 (16) | 0.0532 (7)                       |
| O4  | 0.0206 (4)  | 0.6518 (3)  | 0.29811 (17) | 0.0822 (8)                       |
| H4A | 0.064074    | 0.586678    | 0.297637     | 0.123*                           |
| O2  | -0.0441 (4) | 0.2540 (3)  | 0.21486 (16) | 0.0897 (9)                       |
| H2  | 0.016348    | 0.330320    | 0.214834     | 0.135*                           |
| C7  | 0.3645 (4)  | 0.6053 (3)  | 0.57103 (19) | 0.0457 (7)                       |
| C9  | 0.0451 (4)  | 0.3067 (3)  | 0.4473 (2)   | 0.0469 (7)                       |
| C8  | 0.1507 (4)  | 0.4002 (3)  | 0.5163 (2)   | 0.0490 (7)                       |
| H8  | 0.143775    | 0.382141    | 0.571109     | 0.059*                           |
| C2  | 0.4759 (4)  | 0.7195 (3)  | 0.5508 (2)   | 0.0458 (7)                       |
| C14 | 0.0503 (4)  | 0.3320 (3)  | 0.3637 (2)   | 0.0500 (8)                       |
| C16 | 0.3400 (4)  | 0.2699 (3)  | -0.0509 (2)  | 0.0531 (8)                       |
| C21 | 0.3160 (4)  | 0.3988 (3)  | -0.0583 (2)  | 0.0525 (8)                       |
| C23 | 0.1469 (4)  | 0.6720 (3)  | 0.0803 (2)   | 0.0538 (8)                       |
| C22 | 0.2142 (4)  | 0.5943 (4)  | 0.0084 (2)   | 0.0584 (9)                       |
| H22 | 0.234551    | 0.629736    | -0.040566    | 0.070*                           |
| C28 | 0.1130 (4)  | 0.6197 (3)  | 0.1544 (2)   | 0.0525 (8)                       |
| C12 | -0.1530 (5) | 0.1178 (3)  | 0.3120 (2)   | 0.0645 (9)                       |
| H12 | -0.218773   | 0.053589    | 0.266809     | 0.077*                           |
| C3  | 0.5838 (4)  | 0.8201 (3)  | 0.6109 (2)   | 0.0534 (8)                       |
| C17 | 0.4073 (4)  | 0.1854 (4)  | -0.1138 (2)  | 0.0613 (9)                       |
| C26 | 0.0233 (5)  | 0.8244 (4)  | 0.2207 (3)   | 0.0676 (10)                      |
| H26 | -0.017827   | 0.875467    | 0.267836     | 0.081*                           |
| C27 | 0.0531 (4)  | 0.6990 (4)  | 0.2243 (2)   | 0.0603 (9)                       |
| C13 | -0.0486 (4) | 0.2341 (3)  | 0.2961 (2)   | 0.0586 (9)                       |
| C10 | -0.0661 (4) | 0.1862 (3)  | 0.4616 (2)   | 0.0593 (9)                       |
| H10 | -0.073250   | 0.169793    | 0.516793     | 0.071*                           |
| C20 | 0.3657 (5)  | 0.4421 (4)  | -0.1328 (2)  | 0.0656 (10)                      |
| H20 | 0.351806    | 0.527272    | -0.140140    | 0.079*                           |
| C11 | -0.1625 (5) | 0.0941 (4)  | 0.3947 (3)   | 0.0669 (10)                      |

|      |            |            |             |             |
|------|------------|------------|-------------|-------------|
| H11  | -0.235219  | 0.014899   | 0.404432    | 0.080*      |
| C4   | 0.5836 (5) | 0.8024 (4) | 0.6942 (2)  | 0.0641 (9)  |
| H4   | 0.656723   | 0.867053   | 0.736383    | 0.077*      |
| C24  | 0.1153 (5) | 0.8017 (4) | 0.0781 (3)  | 0.0666 (10) |
| H24  | 0.136398   | 0.837047   | 0.029072    | 0.080*      |
| C6   | 0.3679 (5) | 0.5952 (3) | 0.6565 (2)  | 0.0597 (9)  |
| H6   | 0.294647   | 0.522244   | 0.673039    | 0.072*      |
| C5   | 0.4778 (5) | 0.6914 (4) | 0.7163 (2)  | 0.0710 (11) |
| H5   | 0.481124   | 0.681646   | 0.772972    | 0.085*      |
| C18  | 0.4550 (5) | 0.2344 (4) | -0.1862 (2) | 0.0675 (10) |
| H18  | 0.501793   | 0.180660   | -0.229667   | 0.081*      |
| C25  | 0.0539 (5) | 0.8763 (4) | 0.1473 (3)  | 0.0710 (10) |
| H25  | 0.032795   | 0.961647   | 0.145094    | 0.085*      |
| C19  | 0.4346 (5) | 0.3615 (4) | -0.1952 (2) | 0.0743 (11) |
| H19  | 0.468248   | 0.392695   | -0.244387   | 0.089*      |
| C1   | 0.6961 (5) | 0.9453 (3) | 0.5889 (3)  | 0.0729 (11) |
| H1B  | 0.774499   | 0.916334   | 0.549065    | 0.109*      |
| H1C  | 0.755569   | 1.004995   | 0.640409    | 0.109*      |
| H1D  | 0.629921   | 0.994500   | 0.563320    | 0.109*      |
| C15  | 0.4311 (6) | 0.0463 (4) | -0.1053 (3) | 0.0857 (12) |
| H15A | 0.501966   | 0.057822   | -0.054737   | 0.129*      |
| H15B | 0.482042   | 0.005655   | -0.155138   | 0.129*      |
| H15C | 0.324472   | -0.013470  | -0.100577   | 0.129*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Br1 | 0.0871 (3)  | 0.0575 (2)  | 0.0514 (2)  | 0.01015 (18) | 0.01253 (18) | 0.02160 (16) |
| Br2 | 0.1074 (3)  | 0.0777 (3)  | 0.0517 (2)  | 0.0241 (2)   | 0.0085 (2)   | 0.02912 (19) |
| O1  | 0.0832 (18) | 0.0563 (13) | 0.0492 (13) | -0.0038 (12) | -0.0037 (12) | 0.0181 (11)  |
| O3  | 0.095 (2)   | 0.0653 (14) | 0.0560 (15) | 0.0260 (13)  | 0.0267 (13)  | 0.0235 (12)  |
| N1  | 0.0517 (16) | 0.0429 (13) | 0.0485 (15) | 0.0138 (12)  | 0.0063 (12)  | 0.0120 (11)  |
| N2  | 0.0559 (17) | 0.0566 (15) | 0.0434 (15) | 0.0037 (13)  | 0.0064 (12)  | 0.0133 (12)  |
| O4  | 0.110 (2)   | 0.096 (2)   | 0.0532 (15) | 0.0456 (17)  | 0.0244 (15)  | 0.0214 (14)  |
| O2  | 0.115 (2)   | 0.0826 (18) | 0.0498 (15) | -0.0168 (16) | -0.0007 (14) | 0.0115 (13)  |
| C7  | 0.0526 (19) | 0.0452 (15) | 0.0429 (16) | 0.0179 (14)  | 0.0054 (14)  | 0.0107 (13)  |
| C9  | 0.0467 (19) | 0.0469 (16) | 0.0495 (18) | 0.0145 (14)  | 0.0074 (14)  | 0.0123 (14)  |
| C8  | 0.052 (2)   | 0.0548 (17) | 0.0459 (17) | 0.0204 (15)  | 0.0081 (15)  | 0.0160 (14)  |
| C2  | 0.0482 (19) | 0.0482 (15) | 0.0479 (17) | 0.0212 (14)  | 0.0097 (14)  | 0.0144 (13)  |
| C14 | 0.052 (2)   | 0.0486 (16) | 0.0497 (18) | 0.0118 (14)  | 0.0095 (15)  | 0.0107 (14)  |
| C16 | 0.050 (2)   | 0.0652 (19) | 0.0398 (17) | 0.0051 (16)  | -0.0037 (14) | 0.0126 (15)  |
| C21 | 0.050 (2)   | 0.0598 (18) | 0.0447 (18) | 0.0037 (15)  | 0.0022 (15)  | 0.0155 (15)  |
| C23 | 0.0451 (19) | 0.0603 (18) | 0.0529 (19) | 0.0031 (15)  | 0.0017 (15)  | 0.0158 (15)  |
| C22 | 0.053 (2)   | 0.068 (2)   | 0.054 (2)   | 0.0024 (17)  | 0.0030 (16)  | 0.0263 (17)  |
| C28 | 0.051 (2)   | 0.0578 (18) | 0.0454 (18) | 0.0059 (15)  | 0.0039 (15)  | 0.0117 (15)  |
| C12 | 0.062 (2)   | 0.0557 (19) | 0.066 (2)   | 0.0038 (17)  | 0.0031 (18)  | 0.0029 (16)  |
| C3  | 0.052 (2)   | 0.0503 (17) | 0.059 (2)   | 0.0159 (15)  | 0.0051 (16)  | 0.0100 (15)  |
| C17 | 0.058 (2)   | 0.072 (2)   | 0.050 (2)   | 0.0108 (18)  | -0.0099 (17) | 0.0095 (17)  |

|     |           |             |             |             |              |             |
|-----|-----------|-------------|-------------|-------------|--------------|-------------|
| C26 | 0.059 (2) | 0.072 (2)   | 0.067 (2)   | 0.0160 (19) | 0.0002 (18)  | 0.0036 (18) |
| C27 | 0.057 (2) | 0.066 (2)   | 0.054 (2)   | 0.0095 (17) | 0.0022 (16)  | 0.0113 (16) |
| C13 | 0.063 (2) | 0.0601 (19) | 0.051 (2)   | 0.0121 (17) | 0.0086 (16)  | 0.0112 (16) |
| C10 | 0.056 (2) | 0.0600 (19) | 0.065 (2)   | 0.0098 (17) | 0.0154 (17)  | 0.0250 (17) |
| C20 | 0.082 (3) | 0.070 (2)   | 0.0445 (19) | 0.0119 (19) | 0.0161 (18)  | 0.0191 (17) |
| C11 | 0.057 (2) | 0.059 (2)   | 0.081 (3)   | 0.0024 (17) | 0.012 (2)    | 0.0190 (19) |
| C4  | 0.062 (2) | 0.067 (2)   | 0.057 (2)   | 0.0120 (18) | -0.0103 (17) | 0.0047 (17) |
| C24 | 0.065 (2) | 0.065 (2)   | 0.074 (3)   | 0.0099 (18) | 0.0035 (19)  | 0.0310 (19) |
| C6  | 0.067 (2) | 0.0626 (19) | 0.0497 (19) | 0.0089 (17) | 0.0052 (17)  | 0.0206 (16) |
| C5  | 0.085 (3) | 0.079 (2)   | 0.046 (2)   | 0.008 (2)   | -0.0057 (19) | 0.0187 (18) |
| C18 | 0.065 (2) | 0.086 (3)   | 0.046 (2)   | 0.016 (2)   | 0.0061 (18)  | 0.0049 (18) |
| C25 | 0.067 (3) | 0.059 (2)   | 0.086 (3)   | 0.0149 (19) | 0.003 (2)    | 0.014 (2)   |
| C19 | 0.084 (3) | 0.089 (3)   | 0.052 (2)   | 0.013 (2)   | 0.017 (2)    | 0.026 (2)   |
| C1  | 0.068 (3) | 0.056 (2)   | 0.089 (3)   | 0.0034 (18) | 0.000 (2)    | 0.0165 (19) |
| C15 | 0.106 (4) | 0.092 (3)   | 0.069 (3)   | 0.045 (3)   | 0.002 (2)    | 0.015 (2)   |

*Geometric parameters (Å, °)*

|         |           |          |           |
|---------|-----------|----------|-----------|
| Br1—C2  | 1.903 (3) | C12—C11  | 1.391 (5) |
| Br2—C16 | 1.905 (3) | C12—H12  | 0.9300    |
| O1—C14  | 1.330 (3) | C3—C4    | 1.379 (5) |
| O1—H1   | 0.8200    | C3—C1    | 1.502 (4) |
| O3—C28  | 1.340 (4) | C17—C18  | 1.379 (5) |
| O3—H3   | 0.8200    | C17—C15  | 1.504 (5) |
| N1—C8   | 1.295 (4) | C26—C27  | 1.364 (5) |
| N1—C7   | 1.408 (4) | C26—C25  | 1.388 (5) |
| N2—C22  | 1.277 (4) | C26—H26  | 0.9300    |
| N2—C21  | 1.413 (4) | C10—C11  | 1.361 (5) |
| O4—C27  | 1.370 (4) | C10—H10  | 0.9300    |
| O4—H4A  | 0.8200    | C20—C19  | 1.361 (5) |
| O2—C13  | 1.354 (4) | C20—H20  | 0.9300    |
| O2—H2   | 0.8200    | C11—H11  | 0.9300    |
| C7—C6   | 1.390 (4) | C4—C5    | 1.373 (5) |
| C7—C2   | 1.404 (4) | C4—H4    | 0.9300    |
| C9—C14  | 1.411 (4) | C24—C25  | 1.368 (5) |
| C9—C10  | 1.415 (4) | C24—H24  | 0.9300    |
| C9—C8   | 1.421 (4) | C6—C5    | 1.363 (5) |
| C8—H8   | 0.9300    | C6—H6    | 0.9300    |
| C2—C3   | 1.377 (5) | C5—H5    | 0.9300    |
| C14—C13 | 1.399 (5) | C18—C19  | 1.377 (5) |
| C16—C17 | 1.381 (5) | C18—H18  | 0.9300    |
| C16—C21 | 1.397 (5) | C25—H25  | 0.9300    |
| C21—C20 | 1.388 (4) | C19—H19  | 0.9300    |
| C23—C28 | 1.403 (4) | C1—H1B   | 0.9600    |
| C23—C24 | 1.408 (5) | C1—H1C   | 0.9600    |
| C23—C22 | 1.436 (5) | C1—H1D   | 0.9600    |
| C22—H22 | 0.9300    | C15—H15A | 0.9600    |
| C28—C27 | 1.392 (5) | C15—H15B | 0.9600    |



|             |           |               |           |
|-------------|-----------|---------------|-----------|
| C12—C13     | 1.367 (4) | C15—H15C      | 0.9600    |
| C14—O1—H1   | 109.5     | C26—C27—O4    | 118.4 (3) |
| C28—O3—H3   | 109.5     | C26—C27—C28   | 121.0 (3) |
| C8—N1—C7    | 124.1 (3) | O4—C27—C28    | 120.7 (3) |
| C22—N2—C21  | 123.9 (3) | O2—C13—C12    | 119.2 (3) |
| C27—O4—H4A  | 109.5     | O2—C13—C14    | 120.7 (3) |
| C13—O2—H2   | 109.5     | C12—C13—C14   | 120.1 (3) |
| C6—C7—C2    | 116.9 (3) | C11—C10—C9    | 120.1 (3) |
| C6—C7—N1    | 124.1 (3) | C11—C10—H10   | 120.0     |
| C2—C7—N1    | 119.0 (3) | C9—C10—H10    | 120.0     |
| C14—C9—C10  | 119.1 (3) | C19—C20—C21   | 120.8 (4) |
| C14—C9—C8   | 120.6 (3) | C19—C20—H20   | 119.6     |
| C10—C9—C8   | 120.2 (3) | C21—C20—H20   | 119.6     |
| N1—C8—C9    | 121.8 (3) | C10—C11—C12   | 120.4 (3) |
| N1—C8—H8    | 119.1     | C10—C11—H11   | 119.8     |
| C9—C8—H8    | 119.1     | C12—C11—H11   | 119.8     |
| C3—C2—C7    | 123.4 (3) | C5—C4—C3      | 121.4 (3) |
| C3—C2—Br1   | 119.0 (2) | C5—C4—H4      | 119.3     |
| C7—C2—Br1   | 117.6 (2) | C3—C4—H4      | 119.3     |
| O1—C14—C13  | 118.4 (3) | C25—C24—C23   | 120.7 (3) |
| O1—C14—C9   | 122.3 (3) | C25—C24—H24   | 119.7     |
| C13—C14—C9  | 119.3 (3) | C23—C24—H24   | 119.7     |
| C17—C16—C21 | 123.3 (3) | C5—C6—C7      | 120.4 (3) |
| C17—C16—Br2 | 118.8 (3) | C5—C6—H6      | 119.8     |
| C21—C16—Br2 | 118.0 (3) | C7—C6—H6      | 119.8     |
| C20—C21—C16 | 116.9 (3) | C6—C5—C4      | 121.0 (3) |
| C20—C21—N2  | 124.1 (3) | C6—C5—H5      | 119.5     |
| C16—C21—N2  | 118.9 (3) | C4—C5—H5      | 119.5     |
| C28—C23—C24 | 118.9 (3) | C19—C18—C17   | 121.1 (4) |
| C28—C23—C22 | 120.2 (3) | C19—C18—H18   | 119.4     |
| C24—C23—C22 | 121.0 (3) | C17—C18—H18   | 119.4     |
| N2—C22—C23  | 121.8 (3) | C24—C25—C26   | 119.9 (4) |
| N2—C22—H22  | 119.1     | C24—C25—H25   | 120.1     |
| C23—C22—H22 | 119.1     | C26—C25—H25   | 120.1     |
| O3—C28—C27  | 118.5 (3) | C20—C19—C18   | 120.7 (3) |
| O3—C28—C23  | 122.3 (3) | C20—C19—H19   | 119.6     |
| C27—C28—C23 | 119.1 (3) | C18—C19—H19   | 119.6     |
| C13—C12—C11 | 121.0 (3) | C3—C1—H1B     | 109.5     |
| C13—C12—H12 | 119.5     | C3—C1—H1C     | 109.5     |
| C11—C12—H12 | 119.5     | H1B—C1—H1C    | 109.5     |
| C2—C3—C4    | 116.8 (3) | C3—C1—H1D     | 109.5     |
| C2—C3—C1    | 122.8 (3) | H1B—C1—H1D    | 109.5     |
| C4—C3—C1    | 120.4 (3) | H1C—C1—H1D    | 109.5     |
| C18—C17—C16 | 117.1 (3) | C17—C15—H15A  | 109.5     |
| C18—C17—C15 | 120.2 (4) | C17—C15—H15B  | 109.5     |
| C16—C17—C15 | 122.7 (3) | H15A—C15—H15B | 109.5     |
| C27—C26—C25 | 120.5 (4) | C17—C15—H15C  | 109.5     |

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| C27—C26—H26     | 119.8      | H15A—C15—H15C   | 109.5      |
| C25—C26—H26     | 119.8      | H15B—C15—H15C   | 109.5      |
| C8—N1—C7—C6     | -1.6 (5)   | Br2—C16—C17—C15 | 0.3 (5)    |
| C8—N1—C7—C2     | 179.0 (3)  | C25—C26—C27—O4  | -179.9 (3) |
| C7—N1—C8—C9     | -179.6 (3) | C25—C26—C27—C28 | -0.7 (5)   |
| C14—C9—C8—N1    | -1.1 (5)   | O3—C28—C27—C26  | -178.5 (3) |
| C10—C9—C8—N1    | 178.5 (3)  | C23—C28—C27—C26 | 1.6 (5)    |
| C6—C7—C2—C3     | -0.9 (5)   | O3—C28—C27—O4   | 0.8 (5)    |
| N1—C7—C2—C3     | 178.5 (3)  | C23—C28—C27—O4  | -179.2 (3) |
| C6—C7—C2—Br1    | 179.2 (2)  | C11—C12—C13—O2  | -179.4 (4) |
| N1—C7—C2—Br1    | -1.4 (4)   | C11—C12—C13—C14 | -0.4 (6)   |
| C10—C9—C14—O1   | 178.0 (3)  | O1—C14—C13—O2   | 0.2 (5)    |
| C8—C9—C14—O1    | -2.4 (5)   | C9—C14—C13—O2   | -178.7 (3) |
| C10—C9—C14—C13  | -3.1 (5)   | O1—C14—C13—C12  | -178.8 (3) |
| C8—C9—C14—C13   | 176.5 (3)  | C9—C14—C13—C12  | 2.2 (5)    |
| C17—C16—C21—C20 | -1.0 (5)   | C14—C9—C10—C11  | 2.0 (5)    |
| Br2—C16—C21—C20 | 179.3 (2)  | C8—C9—C10—C11   | -177.5 (3) |
| C17—C16—C21—N2  | -179.7 (3) | C16—C21—C20—C19 | 0.0 (5)    |
| Br2—C16—C21—N2  | 0.6 (4)    | N2—C21—C20—C19  | 178.6 (3)  |
| C22—N2—C21—C20  | 4.1 (5)    | C9—C10—C11—C12  | -0.2 (6)   |
| C22—N2—C21—C16  | -177.3 (3) | C13—C12—C11—C10 | -0.7 (6)   |
| C21—N2—C22—C23  | -178.8 (3) | C2—C3—C4—C5     | -1.5 (6)   |
| C28—C23—C22—N2  | -0.9 (5)   | C1—C3—C4—C5     | 177.7 (4)  |
| C24—C23—C22—N2  | 178.5 (3)  | C28—C23—C24—C25 | 0.6 (5)    |
| C24—C23—C28—O3  | 178.5 (3)  | C22—C23—C24—C25 | -178.9 (3) |
| C22—C23—C28—O3  | -2.1 (5)   | C2—C7—C6—C5     | -1.3 (5)   |
| C24—C23—C28—C27 | -1.5 (5)   | N1—C7—C6—C5     | 179.3 (3)  |
| C22—C23—C28—C27 | 177.9 (3)  | C7—C6—C5—C4     | 2.0 (6)    |
| C7—C2—C3—C4     | 2.3 (5)    | C3—C4—C5—C6     | -0.6 (6)   |
| Br1—C2—C3—C4    | -177.8 (3) | C16—C17—C18—C19 | -0.6 (5)   |
| C7—C2—C3—C1     | -176.9 (3) | C15—C17—C18—C19 | -179.9 (4) |
| Br1—C2—C3—C1    | 3.0 (5)    | C23—C24—C25—C26 | 0.4 (6)    |
| C21—C16—C17—C18 | 1.3 (5)    | C27—C26—C25—C24 | -0.4 (6)   |
| Br2—C16—C17—C18 | -179.0 (2) | C21—C20—C19—C18 | 0.7 (6)    |
| C21—C16—C17—C15 | -179.5 (3) | C17—C18—C19—C20 | -0.3 (6)   |

## 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> |
|-------------------------|-------------|---------------|-----------------------|-------------------------|
| O1—H1...N1              | 0.82        | 1.85          | 2.571 (3)             | 146                     |
| O3—H3...Br2             | 0.82        | 2.86          | 3.499 (2)             | 136                     |
| O3—H3...N2              | 0.82        | 1.85          | 2.560 (3)             | 145                     |
| O4—H4A...O1             | 0.82        | 2.02          | 2.790 (4)             | 157                     |
| O4—H4A...O3             | 0.82        | 2.32          | 2.731 (4)             | 112                     |
| O2—H2...O1              | 0.82        | 2.29          | 2.724 (3)             | 114                     |

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|                         |      |      |           |     |
|-------------------------|------|------|-----------|-----|
| O2—H2...O3              | 0.82 | 2.11 | 2.875 (3) | 156 |
| C8—H8...O4 <sup>i</sup> | 0.93 | 2.54 | 3.383 (4) | 151 |

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