

## Crystal structure of 4-bromo-*N*-(2-bromo-3-nitrobenzyl)-2-nitronaphthalen-1-amine

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In the title compound, C<sub>17</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>4</sub>, the dihedral angle between the planes of the naphthalene system and the benzene ring is 52.86 (8)°. The nitro substituent and the attached naphthalene system are almost coplanar [dihedral angle = 5.6 (4)°], probably as a consequence of an intramolecular N—H···O hydrogen bond with the amine group. The nitro substituent attached to the benzene ring is disordered over two sets of sites with occupancies of 0.694 (3) and 0.306 (3). The major component deviates significantly from the ring plane [dihedral angle = 53.6 (2)°]. In the crystal, the molecules are linked into a three-dimensional array by extensive  $\pi$ – $\pi$  interactions involving both the naphthalene and benzene rings [range of centroid–centroid distances = 3.5295 (16)–3.9629 (18) Å] and C—H···O interactions involving the methylene H atoms and the phenyl-attached nitro group.

**Keywords:** crystal structure; naphthalen-1-amine;  $\pi$ – $\pi$  interactions; hydrogen bonding; arylselenium compounds; photoluminescent selenospirocyclic compounds.

**CCDC reference:** 1015963

### 1. Related literature

For the role of secondary interactions in stabilizing organoselenium compounds, see; Singh *et al.* (2010, 2012); Mugesh & Singh (2000). For the isolation of novel photoluminescent selenospirocyclic compounds *via* intermolecular C—C bond formation, see: Singh *et al.* (2011).

### 2. Experimental

#### 2.1. Crystal data

C<sub>17</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>4</sub>  
 $M_r = 481.11$   
 Triclinic,  $P\bar{1}$   
 $a = 8.3675$  (4) Å  
 $b = 8.5812$  (5) Å  
 $c = 12.2691$  (5) Å  
 $\alpha = 76.973$  (4)°  
 $\beta = 81.053$  (4)°  
 $\gamma = 76.302$  (5)°  
 $V = 829.00$  (8) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.92$  mm<sup>-1</sup>  
 $T = 123$  K  
 0.44 × 0.32 × 0.12 mm

#### 2.2. Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer  
 Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)  
 $T_{\min} = 0.345$ ,  $T_{\max} = 1.000$   
 12164 measured reflections  
 6700 independent reflections  
 4118 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

#### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.129$   
 $S = 1.02$   
 6700 reflections  
 246 parameters  
 1 restraint  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 1.04$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.77$  e Å<sup>-3</sup>

**Table 1**  
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···O2	0.84 (3)	1.91 (3)	2.624 (3)	141 (3)
C12—H12B···O4A <sup>i</sup>	0.99	2.54	3.532 (4)	177
C12—H12B···O4B <sup>i</sup>	0.99	2.61	3.462 (8)	144

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

### Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5325).

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## References

Agilent (2012). *CrysAlis PRO* and *CrysAlis RED*. Agilent Technologies, Yarnton, England.

- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.  
Mugesh, G. & Singh, H. B. (2000). *Chem. Soc. Rev.* **29**, 347–357.  
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.  
Singh, V. P., Singh, H. B. & Butcher, R. J. (2010). *Eur. J. Inorg. Chem.* pp. 637–647.  
Singh, V. P., Singh, H. B. & Butcher, R. J. (2011). *Chem. Commun.* **47**, 7221–7223.  
Singh, V. P., Singh, P., Singh, H. B. & Butcher, R. J. (2012). *Tetrahedron Lett.* **53**, 4591–4594.

## supporting information

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## Crystal structure of 4-bromo-*N*-(2-bromo-3-nitrobenzyl)-2-nitronaphthalen-1-amine

Vijay P. Singh, Krishnan Venkateshwaran, Harkesh B. Singh and Ray J. Butcher

### S1. Comment

Arylselenium compounds having one *ortho*-coordinating group have been widely studied as reagents in organic synthesis, glutathione peroxidase mimics, and precursors for the synthesis of macrocycles (Singh *et al.*, 2012; Mugesh & Singh, 2000). Introduction of a second *ortho*-coordinating group towards selenium leads to interesting reactivity of the selenium derivatives and isolation of unusual species (Singh *et al.*, 2010). Recently, we reported the isolation of novel photoluminescent selenospirocyclic compounds *via* intermolecular C—C bond formation (Singh *et al.*, 2011). In continuation of this research, we attempted the synthesis of naphthylamine based spirocyclic compounds. However, the reaction led to the isolation of 4-bromo-*N*-(2-bromo-3-nitrobenzyl)-2-nitronaphthalen-1-amine (**2**) instead of the desired spiro-compound (**3**) (Fig. 1).

In the structure of the title compound, Fig. 2, the naphthyl nitro substituent is almost coplanar with the naphthyl ring (dihedral angle = 5.6 (4)°) probably as a consequence of an intramolecular hydrogen bond with the N—H moiety. However, the nitro substituent attached to the benzene deviates significantly from the ring plane (dihedral angle = 53.6 (2)° for the major component); this is disordered with occupancies of 0.694 (3) and 0.306 (3). The dihedral angle between the two ring systems is 52.86 (8)°. The molecules are linked into a three-dimensional array, Fig. 3, by extensive  $\pi$ – $\pi$  interactions involving both the naphthyl ring (Cg1; C1, C2, C3, C4, C5, C10; Cg2; C5, C6, C7, C8, C9, C10) and benzene ring (Cg3; C13, C14, C15, C16, C17, C18), see Table 1, and, in addition, there are weak intermolecular C—H $\cdots$ O interactions involving the methylene H atoms and the benzenenitro group, Table 2.

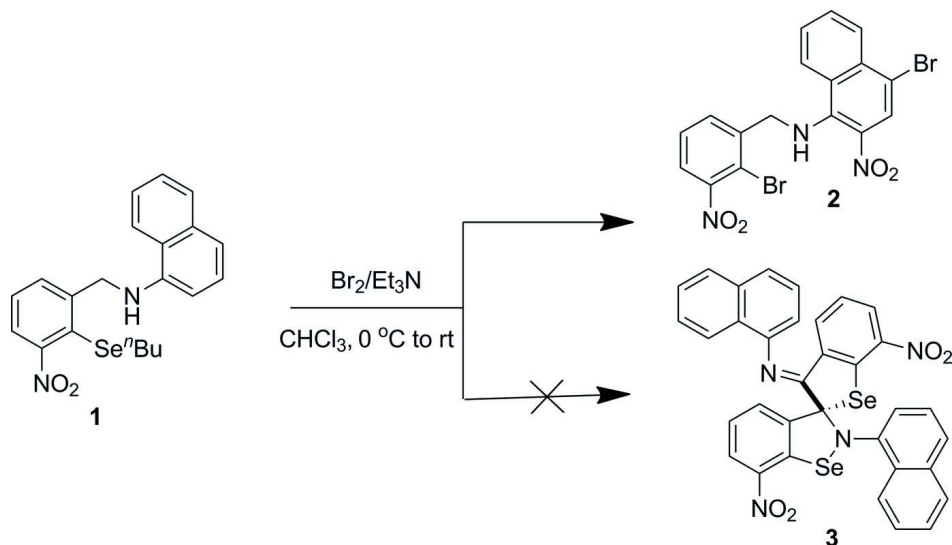
### S2. Experimental

Referring to Fig. 1, to a stirred solution of selenide **1** (0.400 g 1 mmol in 3 mL CHCl<sub>3</sub>) at 0° C, was added bromine (0.05 ml in 1 mL CHCl<sub>3</sub>). After 30 mins a yellow precipitate was formed. Stirring was continued for further 30 mins, Et<sub>3</sub>N (0.140 ml) added and the stirring continued for an additional 6 h. After completion of the reaction, the reaction mixture was poured into water and extracted with CHCl<sub>3</sub> (2 × 30 mL). The combined organic layers were dried over sodium sulfate and evaporated on a rotary evaporator to get a brown solid. Yield: 0.230 g (49 %); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  [ppm] = 7.57–7.83 (m, 6H), 8.12 (s, CH, 1H), 8.29–8.32 (d,  $J$  = 8.43 Hz, 1H), 8.55–8.58 (dd,  $J$  = 0.73, 7.33 Hz, 1H), 8.66–8.69 (dd,  $J$  = 0.73, 8.06 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  [ppm] = 122.7, 123.8, 125.3, 128.1, 128.2, 128.3, 128.5, 129.2, 130.0, 132.2, 132.4, 133.2, 133.4, 135.8, 138.2, 142.5, 164.9. IR (KBr): 3455, 2924, 1666, 1510, 1374, 1296, 768, 734 cm<sup>-1</sup>.

#### S2.1. Refinement

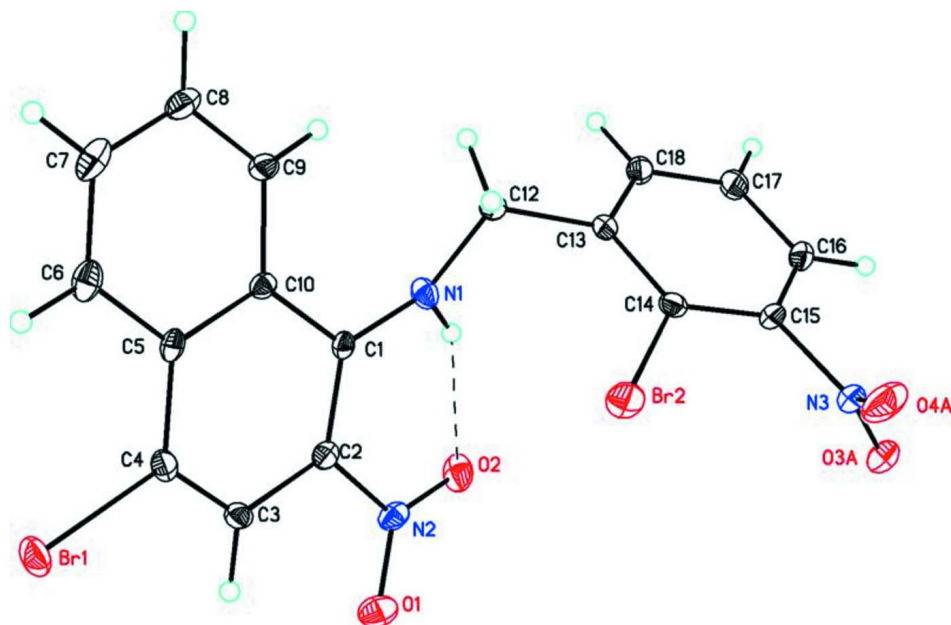
C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.95–0.99 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$ . The N-bound H atom was refined freely. One of the nitro groups was disordered over two conformations with occupancies of 0.694 (3) and 0.306 (4). The two conformers were

constrained to have similar metrical parameters. Highest residual electron density peak;  $1.02 \text{ e}/\text{\AA}^3$  is  $0.74 \text{ \AA}$  from Br2, and the deepest hole of  $-0.81 \text{ e}/\text{\AA}^3$  is  $0.65 \text{ \AA}$  from Br1. Twelve reflections were removed from the final refinement owing to poor agreement.



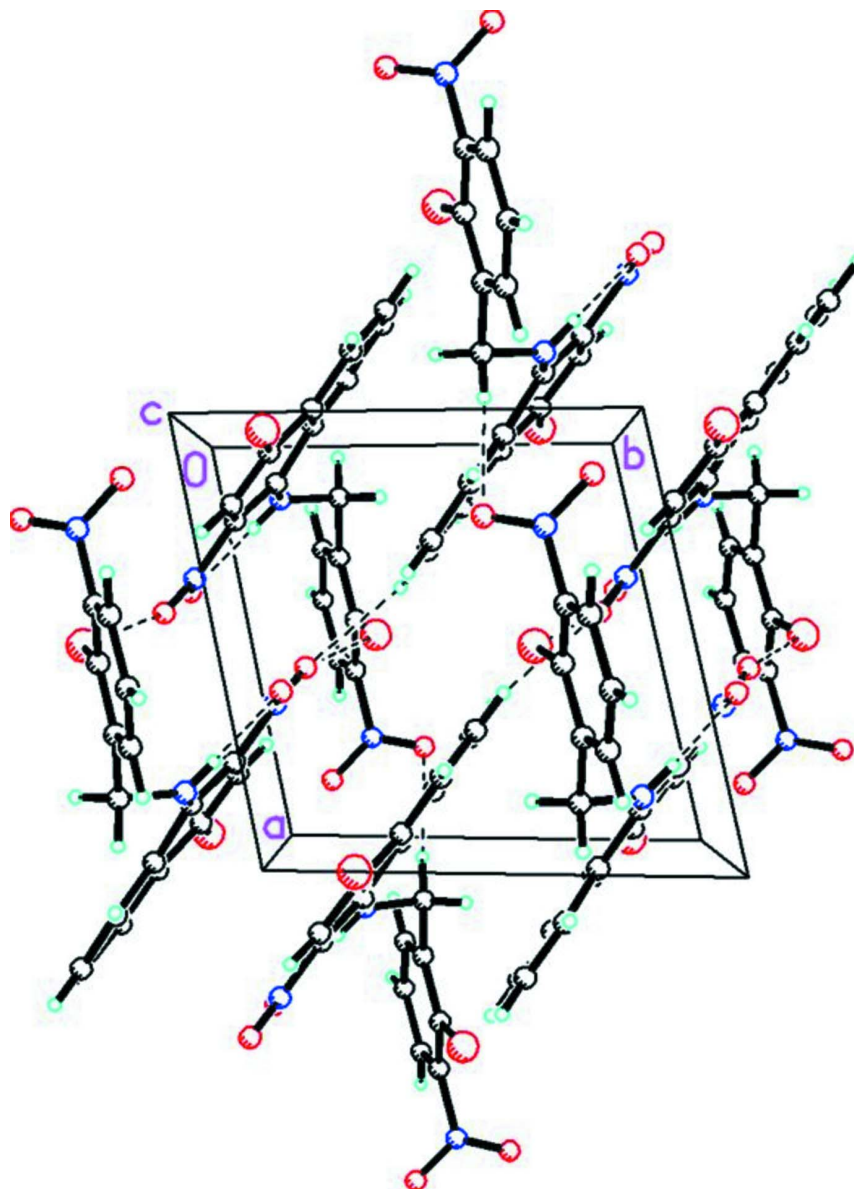
**Figure 1**

The reaction scheme.



**Figure 2**

The molecular structure of  $\text{C}_{17}\text{H}_{11}\text{Br}_2\text{N}_3\text{O}_4$  showing the numbering scheme and 30% probability displacement ellipsoids and the intramolecular N—H...O hydrogen bond (shown as a dashed bond).



**Figure 3**

The molecular packing for  $C_{17}H_{11}Br_2N_3O_4$  viewed along the  $c$  axis showing the linking of the molecules into a three-dimensional array by  $\pi$ - $\pi$  interactions as well as a network of C—H $\cdots$ O interactions (shown as dashed bonds).

#### 4-Bromo-*N*-(2-bromo-3-nitrobenzyl)-2-nitronaphthalen-1-amine

##### Crystal data

$C_{17}H_{11}Br_2N_3O_4$

$M_r = 481.11$

Triclinic,  $P\bar{1}$

$a = 8.3675$  (4) Å

$b = 8.5812$  (5) Å

$c = 12.2691$  (5) Å

$\alpha = 76.973$  (4)°

$\beta = 81.053$  (4)°

$\gamma = 76.302$  (5)°

$V = 829.00$  (8) Å<sup>3</sup>

$Z = 2$

$F(000) = 472$

$D_x = 1.927$  Mg m<sup>-3</sup>

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

Cell parameters from 3926 reflections

$\theta = 5.0$ – $34.9$ °

$\mu = 4.92 \text{ mm}^{-1}$   
 $T = 123 \text{ K}$

Plate, orange  
 $0.44 \times 0.32 \times 0.12 \text{ mm}$

*Data collection*

Agilent Xcalibur (Ruby, Gemini)  
 diffractometer  
 Detector resolution:  $10.5081 \text{ pixels mm}^{-1}$   
 $\omega$  scans  
 Absorption correction: multi-scan  
 (CrysAlis PRO; Agilent, 2012)  
 $T_{\min} = 0.345$ ,  $T_{\max} = 1.000$   
 12164 measured reflections

6700 independent reflections  
 4118 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\max} = 35.0^\circ$ ,  $\theta_{\min} = 5.0^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -12 \rightarrow 13$   
 $l = -19 \rightarrow 19$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.129$   
 $S = 1.02$   
 6700 reflections  
 246 parameters  
 1 restraint  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.3384P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.04 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.77 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.52119 (4)	0.68126 (4)	0.76444 (2)	0.03410 (10)	
Br2	0.98711 (4)	0.82225 (4)	0.23405 (3)	0.03346 (10)	
O1	0.9351 (3)	0.3484 (3)	0.5032 (2)	0.0374 (6)	
O2	0.8810 (3)	0.4048 (3)	0.3315 (2)	0.0346 (5)	
O3A	1.3573 (4)	0.6322 (4)	0.0114 (3)	0.0334 (7)	0.694 (3)
O4A	1.2701 (4)	0.8769 (5)	0.0461 (4)	0.0480 (10)	0.694 (3)
O3B	1.3147 (8)	0.8513 (9)	-0.0408 (7)	0.0334 (7)	0.306 (3)
O4B	1.3038 (10)	0.6768 (10)	0.1138 (8)	0.0480 (10)	0.306 (3)
N1	0.6518 (3)	0.6613 (3)	0.2639 (2)	0.0230 (5)	
H1N	0.724 (4)	0.577 (4)	0.254 (3)	0.027 (9)*	
N2	0.8518 (3)	0.4286 (3)	0.4272 (2)	0.0240 (5)	
N3	1.2471 (3)	0.7536 (3)	0.0266 (2)	0.0276 (6)	
C1	0.6183 (3)	0.6659 (3)	0.3756 (2)	0.0171 (5)	
C2	0.7114 (3)	0.5555 (3)	0.4567 (2)	0.0196 (5)	
C3	0.6804 (3)	0.5624 (3)	0.5728 (2)	0.0211 (5)	
H3A	0.7467	0.4854	0.6252	0.025*	
C4	0.5575 (3)	0.6778 (4)	0.6087 (2)	0.0216 (5)	
C5	0.4516 (3)	0.7931 (3)	0.5332 (2)	0.0183 (5)	

C6	0.3170 (3)	0.9116 (4)	0.5696 (3)	0.0264 (6)
H6A	0.2998	0.9217	0.6463	0.032*
C7	0.2119 (3)	1.0113 (4)	0.4962 (3)	0.0292 (7)
H7A	0.1240	1.0917	0.5220	0.035*
C8	0.2318 (3)	0.9967 (4)	0.3842 (3)	0.0267 (6)
H8A	0.1552	1.0642	0.3346	0.032*
C9	0.3622 (3)	0.8845 (3)	0.3448 (2)	0.0216 (5)
H9A	0.3741	0.8749	0.2682	0.026*
C10	0.4788 (3)	0.7832 (3)	0.4170 (2)	0.0171 (5)
C12	0.6425 (3)	0.8012 (4)	0.1692 (2)	0.0224 (6)
H12A	0.6430	0.9014	0.1961	0.027*
H12B	0.5383	0.8185	0.1351	0.027*
C13	0.7896 (3)	0.7678 (3)	0.0821 (2)	0.0196 (5)
C14	0.9489 (3)	0.7762 (3)	0.0981 (2)	0.0197 (5)
C15	1.0768 (3)	0.7462 (4)	0.0142 (2)	0.0220 (6)
C16	1.0535 (3)	0.7066 (4)	-0.0846 (2)	0.0265 (6)
H16A	1.1437	0.6861	-0.1406	0.032*
C17	0.8958 (4)	0.6977 (4)	-0.1002 (2)	0.0286 (6)
H17A	0.8765	0.6709	-0.1674	0.034*
C18	0.7659 (3)	0.7280 (4)	-0.0171 (2)	0.0251 (6)
H18A	0.6581	0.7213	-0.0284	0.030*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.03423 (17)	0.0569 (2)	0.01698 (15)	-0.01906 (15)	0.00074 (12)	-0.01145 (14)
Br2	0.03155 (17)	0.0494 (2)	0.02682 (17)	-0.01218 (14)	-0.00825 (13)	-0.01525 (14)
O1	0.0319 (11)	0.0295 (13)	0.0449 (15)	0.0057 (9)	-0.0109 (11)	-0.0035 (11)
O2	0.0336 (12)	0.0256 (12)	0.0354 (13)	0.0041 (9)	0.0090 (10)	-0.0068 (10)
O3A	0.0187 (13)	0.0379 (18)	0.0399 (18)	-0.0008 (12)	-0.0021 (12)	-0.0062 (14)
O4A	0.0293 (16)	0.042 (2)	0.077 (3)	-0.0142 (15)	-0.0194 (17)	-0.0033 (19)
O3B	0.0187 (13)	0.0379 (18)	0.0399 (18)	-0.0008 (12)	-0.0021 (12)	-0.0062 (14)
O4B	0.0293 (16)	0.042 (2)	0.077 (3)	-0.0142 (15)	-0.0194 (17)	-0.0033 (19)
N1	0.0283 (12)	0.0210 (13)	0.0178 (11)	-0.0034 (10)	0.0014 (9)	-0.0045 (9)
N2	0.0187 (10)	0.0158 (12)	0.0353 (14)	-0.0023 (9)	-0.0050 (10)	-0.0002 (10)
N3	0.0184 (11)	0.0345 (16)	0.0282 (13)	-0.0085 (11)	-0.0050 (10)	0.0023 (11)
C1	0.0144 (10)	0.0196 (13)	0.0179 (12)	-0.0063 (9)	0.0009 (9)	-0.0039 (10)
C2	0.0168 (11)	0.0173 (13)	0.0237 (13)	-0.0033 (10)	-0.0009 (10)	-0.0032 (10)
C3	0.0202 (12)	0.0237 (14)	0.0189 (13)	-0.0079 (10)	-0.0044 (10)	0.0020 (10)
C4	0.0213 (12)	0.0310 (15)	0.0162 (12)	-0.0127 (11)	-0.0005 (10)	-0.0056 (11)
C5	0.0145 (10)	0.0204 (13)	0.0220 (13)	-0.0078 (9)	0.0028 (9)	-0.0075 (10)
C6	0.0230 (13)	0.0292 (16)	0.0311 (16)	-0.0082 (11)	0.0046 (12)	-0.0163 (12)
C7	0.0185 (12)	0.0239 (16)	0.046 (2)	-0.0037 (11)	0.0035 (12)	-0.0147 (14)
C8	0.0173 (12)	0.0191 (14)	0.0401 (18)	-0.0009 (10)	-0.0033 (12)	-0.0016 (12)
C9	0.0164 (11)	0.0251 (15)	0.0229 (13)	-0.0046 (10)	-0.0052 (10)	-0.0018 (11)
C10	0.0148 (10)	0.0152 (12)	0.0206 (13)	-0.0032 (9)	-0.0023 (9)	-0.0021 (9)
C12	0.0187 (11)	0.0292 (15)	0.0179 (13)	-0.0031 (10)	-0.0026 (10)	-0.0033 (11)
C13	0.0185 (11)	0.0246 (14)	0.0149 (12)	-0.0050 (10)	-0.0023 (9)	-0.0010 (10)

C14	0.0221 (12)	0.0208 (14)	0.0167 (12)	-0.0060 (10)	-0.0062 (10)	-0.0002 (10)
C15	0.0141 (11)	0.0264 (15)	0.0244 (14)	-0.0056 (10)	-0.0039 (10)	-0.0003 (11)
C16	0.0183 (12)	0.0381 (18)	0.0205 (14)	-0.0055 (12)	0.0021 (10)	-0.0036 (12)
C17	0.0287 (14)	0.0424 (19)	0.0159 (13)	-0.0087 (13)	-0.0025 (11)	-0.0066 (12)
C18	0.0205 (12)	0.0385 (18)	0.0185 (14)	-0.0105 (12)	-0.0042 (10)	-0.0039 (12)

*Geometric parameters (Å, °)*

Br1—C4	1.893 (3)	C6—C7	1.364 (5)
Br2—C14	1.887 (3)	C6—H6A	0.9500
O1—N2	1.231 (3)	C7—C8	1.388 (5)
O2—N2	1.214 (3)	C7—H7A	0.9500
O3A—N3	1.245 (4)	C8—C9	1.378 (4)
O4A—N3	1.199 (4)	C8—H8A	0.9500
O3B—N3	1.214 (7)	C9—C10	1.419 (4)
O4B—N3	1.224 (9)	C9—H9A	0.9500
N1—C1	1.363 (3)	C12—C13	1.517 (4)
N1—C12	1.467 (4)	C12—H12A	0.9900
N1—H1N	0.85 (3)	C12—H12B	0.9900
N2—C2	1.461 (3)	C13—C18	1.390 (4)
N3—C15	1.474 (3)	C13—C14	1.398 (4)
C1—C2	1.400 (4)	C14—C15	1.386 (4)
C1—C10	1.457 (4)	C15—C16	1.383 (4)
C2—C3	1.420 (4)	C16—C17	1.385 (4)
C3—C4	1.344 (4)	C16—H16A	0.9500
C3—H3A	0.9500	C17—C18	1.388 (4)
C4—C5	1.432 (4)	C17—H17A	0.9500
C5—C6	1.417 (4)	C18—H18A	0.9500
C5—C10	1.426 (4)		
C1—N1—C12	127.2 (2)	C9—C8—C7	120.2 (3)
C1—N1—H1N	111 (2)	C9—C8—H8A	119.9
C12—N1—H1N	116 (2)	C7—C8—H8A	119.9
O2—N2—O1	122.8 (3)	C8—C9—C10	121.0 (3)
O2—N2—C2	120.1 (2)	C8—C9—H9A	119.5
O1—N2—C2	117.1 (3)	C10—C9—H9A	119.5
O3B—N3—O4B	122.8 (5)	C9—C10—C5	118.2 (2)
O4A—N3—O3A	125.1 (3)	C9—C10—C1	121.3 (2)
O4A—N3—C15	118.2 (3)	C5—C10—C1	120.5 (2)
O3B—N3—C15	119.2 (4)	N1—C12—C13	109.3 (2)
O4B—N3—C15	117.1 (4)	N1—C12—H12A	109.8
O3A—N3—C15	116.7 (3)	C13—C12—H12A	109.8
N1—C1—C2	122.2 (2)	N1—C12—H12B	109.8
N1—C1—C10	121.2 (2)	C13—C12—H12B	109.8
C2—C1—C10	116.6 (2)	H12A—C12—H12B	108.3
C1—C2—C3	122.5 (2)	C18—C13—C14	118.7 (2)
C1—C2—N2	122.3 (3)	C18—C13—C12	119.2 (2)
C3—C2—N2	115.1 (3)	C14—C13—C12	122.1 (3)



C4—C3—C2	120.1 (3)	C15—C14—C13	118.8 (3)
C4—C3—H3A	120.0	C15—C14—Br2	121.3 (2)
C2—C3—H3A	120.0	C13—C14—Br2	119.9 (2)
C3—C4—C5	121.8 (3)	C16—C15—C14	122.6 (2)
C3—C4—Br1	118.3 (2)	C16—C15—N3	116.3 (2)
C5—C4—Br1	119.9 (2)	C14—C15—N3	121.1 (3)
C6—C5—C10	118.8 (3)	C15—C16—C17	118.5 (3)
C6—C5—C4	122.8 (3)	C15—C16—H16A	120.7
C10—C5—C4	118.4 (2)	C17—C16—H16A	120.7
C7—C6—C5	121.0 (3)	C16—C17—C18	119.7 (3)
C7—C6—H6A	119.5	C16—C17—H17A	120.2
C5—C6—H6A	119.5	C18—C17—H17A	120.2
C6—C7—C8	120.8 (3)	C17—C18—C13	121.7 (3)
C6—C7—H7A	119.6	C17—C18—H18A	119.2
C8—C7—H7A	119.6	C13—C18—H18A	119.2
C12—N1—C1—C2	-141.9 (3)	N1—C1—C10—C9	7.0 (4)
C12—N1—C1—C10	40.5 (4)	C2—C1—C10—C9	-170.8 (2)
N1—C1—C2—C3	178.1 (2)	N1—C1—C10—C5	-176.1 (2)
C10—C1—C2—C3	-4.1 (4)	C2—C1—C10—C5	6.2 (3)
N1—C1—C2—N2	0.6 (4)	C1—N1—C12—C13	138.6 (3)
C10—C1—C2—N2	178.3 (2)	N1—C12—C13—C18	105.6 (3)
O2—N2—C2—C1	-7.7 (4)	N1—C12—C13—C14	-74.5 (3)
O1—N2—C2—C1	173.1 (2)	C18—C13—C14—C15	0.6 (4)
O2—N2—C2—C3	174.6 (2)	C12—C13—C14—C15	-179.2 (3)
O1—N2—C2—C3	-4.6 (3)	C18—C13—C14—Br2	-177.7 (2)
C1—C2—C3—C4	0.2 (4)	C12—C13—C14—Br2	2.4 (4)
N2—C2—C3—C4	177.9 (2)	C13—C14—C15—C16	-0.6 (4)
C2—C3—C4—C5	1.9 (4)	Br2—C14—C15—C16	177.7 (2)
C2—C3—C4—Br1	179.86 (19)	C13—C14—C15—N3	179.9 (3)
C3—C4—C5—C6	177.4 (3)	Br2—C14—C15—N3	-1.7 (4)
Br1—C4—C5—C6	-0.6 (3)	O4A—N3—C15—C16	125.2 (4)
C3—C4—C5—C10	0.2 (4)	O3B—N3—C15—C16	60.9 (6)
Br1—C4—C5—C10	-177.74 (18)	O4B—N3—C15—C16	-129.3 (6)
C10—C5—C6—C7	2.0 (4)	O3A—N3—C15—C16	-52.1 (4)
C4—C5—C6—C7	-175.2 (3)	O4A—N3—C15—C14	-55.3 (4)
C5—C6—C7—C8	1.5 (4)	O3B—N3—C15—C14	-119.6 (6)
C6—C7—C8—C9	-2.3 (4)	O4B—N3—C15—C14	50.2 (6)
C7—C8—C9—C10	-0.5 (4)	O3A—N3—C15—C14	127.4 (3)
C8—C9—C10—C5	3.9 (4)	C14—C15—C16—C17	0.4 (5)
C8—C9—C10—C1	-179.1 (2)	N3—C15—C16—C17	179.8 (3)
C6—C5—C10—C9	-4.6 (4)	C15—C16—C17—C18	-0.1 (5)
C4—C5—C10—C9	172.7 (2)	C16—C17—C18—C13	0.2 (5)
C6—C5—C10—C1	178.4 (2)	C14—C13—C18—C17	-0.4 (4)
C4—C5—C10—C1	-4.3 (4)	C12—C13—C18—C17	179.4 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N $\cdots$ O2	0.84 (3)	1.91 (3)	2.624 (3)	141 (3)
C12—H12A $\cdots$ O3B <sup>i</sup>	0.99	2.57	3.117 (8)	115
C12—H12B $\cdots$ O4A <sup>ii</sup>	0.99	2.54	3.532 (4)	177
C12—H12B $\cdots$ O4B <sup>ii</sup>	0.99	2.61	3.462 (8)	144

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

 *$\pi$ - $\pi$  interactions* ( $\text{\AA}$ )

Ring 1	Ring 2	Distance	Perpendicular distance	Slippage	Symmetry
Cg1	Cg1	3.5295 (16)	3.3867 (11)	0.94	1-x,1-y,1-z
Cg2	Cg2	3.8868 (15)	3.3859 (12)	1.91	1-x,-y,1-z
Cg3	Cg3	3.9629 (18)	3.5873 (12)	1.68	-x,1-y,2-z