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# *N*-{1-[(3-Bromopropyl)aminocarbonyl]-ethyl}-2-(2-nitrobenzenesulfonamido)-propionamide

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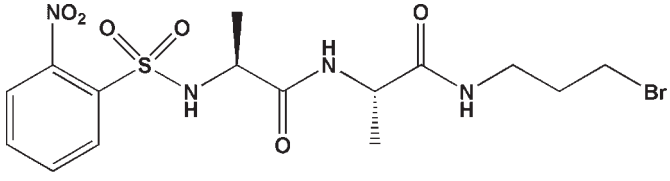
Key indicators: single-crystal X-ray study; $T$ = 292 K; mean $\sigma$(C–C) = 0.007 Å; $R$ factor = 0.047; $wR$ factor = 0.138; data-to-parameter ratio = 16.6.

In the title compound, $C_{15}H_{21}BrN_4O_6S$, all three NH groups are involved in intermolecular N—H···O interactions which, together with two intermolecular C—H···O contacts, lead to a continuous antiparallel $\beta$-sheet structure. There are no $\pi$–$\pi$ interactions between molecules, and two C—H···$\pi$ interactions primarily govern the linkage between sheets.

## Related literature

For conformationally restricted peptide analogues, see: Belvisi *et al.* (2000); Ripka *et al.* (1993). For C-H···$\pi$ interactions in crystals and peptides, see: Ciunik *et al.* (1998); Görbitz (1989); Nishio (2004); Nishio & Hirota (1989). For the correlation between peptide sequences and folds, see: Venkatraman *et al.* (2001); Wilmot & Thornton (1988). For bond angles in $\beta$-strand structures, see: Loughlin *et al.* (2004).



## Experimental

### *Crystal data*

$C_{15}H_{21}BrN_4O_6S$
$M_r$ = 465.33
Orthorhombic, $P2_12_12_1$
$a$ = 9.4467 (4) Å
$b$ = 12.7438 (5) Å
$c$ = 17.3257 (7) Å
$V$ = 2085.79 (15) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.11 mm$^{-1}$
$T$ = 292 K
0.30 × 0.20 × 0.10 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min}$ = 0.571, $T_{max}$ = 0.817
33853 measured reflections
4107 independent reflections
3007 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.138
$S$ = 1.10
4107 reflections
247 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.51 e Å$^{-3}$
Absolute structure: Flack (1983), 1763 Friedel pairs
Flack parameter: −0.011 (13)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$A$···O6$^{i}$ | 0.86 | 2.07 | 2.884 (4) | 158 |
| N3—H3$A$···O6 | 0.86 | 2.54 | 2.829 (4) | 100 |
| N3—H3$A$···O5$^{ii}$ | 0.86 | 2.07 | 2.899 (4) | 162 |
| N4—H4$A$···O4$^{i}$ | 0.86 | 2.35 | 3.165 (5) | 159 |
| C2—H2···O4 | 0.93 | 2.49 | 2.867 (6) | 104 |
| C7—H7···O5$^{ii}$ | 0.98 | 2.34 | 3.193 (5) | 145 |
| C10—H10···O4$^{i}$ | 0.98 | 2.51 | 3.431 (5) | 156 |
| C13—H13$A$···O6 | 0.97 | 2.46 | 2.802 (6) | 100 |
| C13—H13$B$···O3$^{iii}$ | 0.97 | 2.60 | 3.496 (6) | 154 |
| C11—H11$A$···$Cg$ | 3.39 | 0.96 | 3.922 (6) | 117 |
| C11—H11$B$···$Cg^{i}$ | 3.27 | 0.96 | 3.857 (6) | 121 |

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (iii) $x, y-1, z$. $Cg$ is the centroid of the C1–C6 ring.

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1999) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2284).

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# supporting information

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## *N*-{1-[(3-Bromopropyl)aminocarbonyl]ethyl}-2-(2-nitrobenzenesulfonamido)-propionamide

**Ravula Thirupathi, Damodara N. Reddy, S. Brinda and Erode N. Prabhakaran**

### S1. Comment

The title compound is a precursor for making conformationally restricted dipeptide analogues, which are essential for many molecular recognition events including interactions between antigens and antibodies, peptide hormones and their receptors, and enzymes and their corresponding substrates (Ripka *et al.*, 1993; Belvisi *et al.*, 2000). The dipeptide sequence Ala-Ala has a low frequency of appearance in the conformationally ordered regions of polypeptides (Wilmot & Thornton, 1988; Venkatraman *et al.*, 2001). The sulfonamide group is known to render conformational ordering in peptides and many sulfonamides are crystalline in nature. The title compound was synthesized to investigate the ordering rendered to Ala-Ala dipeptide by the N-nosyl (2-nitro-benzenesulfonylamino) protecting group. In the crystal structure all the three NH groups of the molecule are involved in intermolecular N—H···O interactions.

The two adjacent amide N-H bonds, $N_3$—$H_3$ and $N_4$—$H_4$, that flank the C- terminal alanine in the title compound are antiperiplanar to each other. The phi, psi angles for the C-terminal alanine are phi = -151.9 (5)°, psi = 130.4 (2)°. These angles and the H3-N3-N4-H4 dihedral angle (166.1 (3)°) are within the limits of those found in b-strand structures (Loughlin *et al.*, 2004). On the other hand, the two adjacent N-H bonds $N_2$—$H_2$ and $N_3$—$H_3$ that flank the N-terminal alanine are slightly distorted away from ideal antiperiplanarity (H2-N2-N3-H3 dihedral angle = 150.2 (5)°). The phi, psi angles for the N-terminal alanine are phi = 95.6 (2)°, psi = 137.8 (7)°. The distortion from the ideal phi value for a beta-strand near N2 is probably due to the fact that N2 is bonded to a sulfonyl group rather than an acyl group.

The strands are arranged in a head-to-tail fashion, with three intermolecular N—H···O interactions and two intermolecular C—H···O interactions (Table 1). These interactions are between adjacent strands and assist in forming a continuous beta-sheet structure. The C1—S1—N2—C7 torsion angle is 62.9 (3)°. This orients the phenyl ring at a dihedral angle of 73.9 (1)° from the mean plane of the rest of the molecule. The crystal structure is stabilized by two C—H···$\pi$ interactions. One is intermolecular ($C_{11}$—$C_g$ = 3.85 A°, Cg: the centroid of the phenyl ring) and the other is intramolecular ($C_{11}$—$C_g$ = 3.92 A°). There are no $\pi$–$\pi$ interactions between the phenyl rings and the interactions between the sheets are solely governed by the C—H···$\pi$ interactions.

### S2. Experimental

To a stirring solution of 2-[2′-(2-nitrosulfonylamido)-propionamido]-propanoic acid (650 mg, 1.88 mmol) in THF (10 ml) at 258 K was added *N*-methyl morpholene (0.31 ml, 2.82 mmol) followed by ethylchloroformate (0.18 ml,1.93 mmol) under $N_2$ atmosphere. After two minutes a solution of 3-bromopropan-1-ammonium bromide (536 mg, 2.44 mmol) and *N*-Methyl morpholene (0.51 ml, 4.7 mmol) in a mixture of DMF/THF (1.5/3 ml) were added to the mixture and stirred for 10 min. The reaction mixture was warmed to room temperature and stirred for further 8 h. THF was removed under reduced pressure and the resulting residue was diluted with EtOAc (10 ml) and washed with saturated aqueous citric acid solution (5 ml), saturated aqueous $NaHCO_3$ (5 ml) solution and dried (anhydrous $Na_2SO_4$). The solvent was removed

under reduced pressure and the resulting residue was purified by silica gel flash column chromatography (EtOAc/Hexane:1/2) to obtain the title compound as a colorless solid 392 mg (0.84 mmol, 45%) (m.p. 404 K). Needle like crystals were obtained for the isolated compound by slow evaporation at room temperature from a solution in 2-propanol (2.1 m*M*).

### S3. Refinement

All the H atoms were positioned geometrically with C—H bond lengths of 0.93 (3)–0.97 (3) Å, and refined using a riding model approximation with $U_{iso}$(H) = 1.2 $U_{eq}$(C) or 1.5 $U_{eq}$(C) for methyl H atoms.

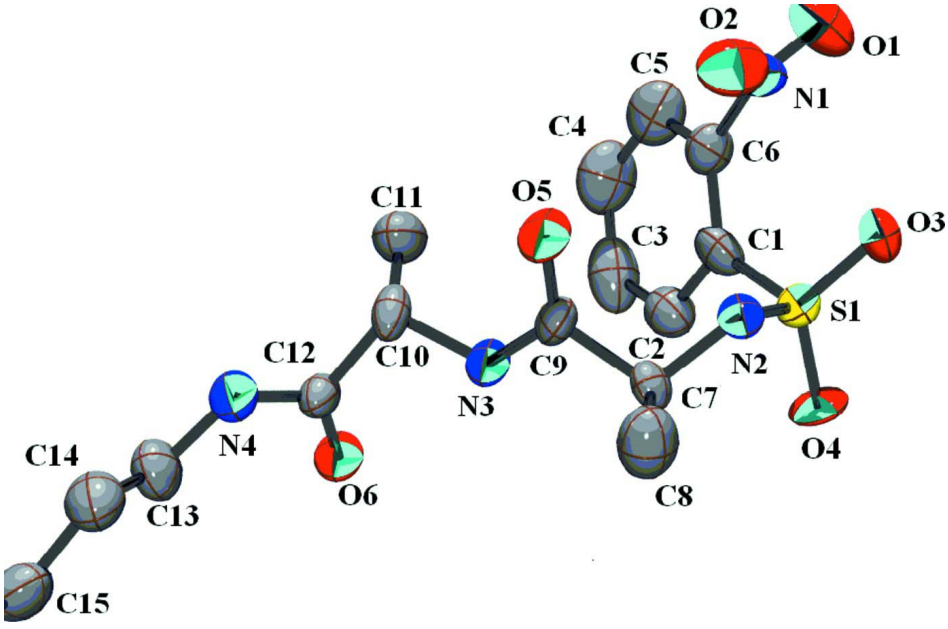


**Figure 1**

View of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity.

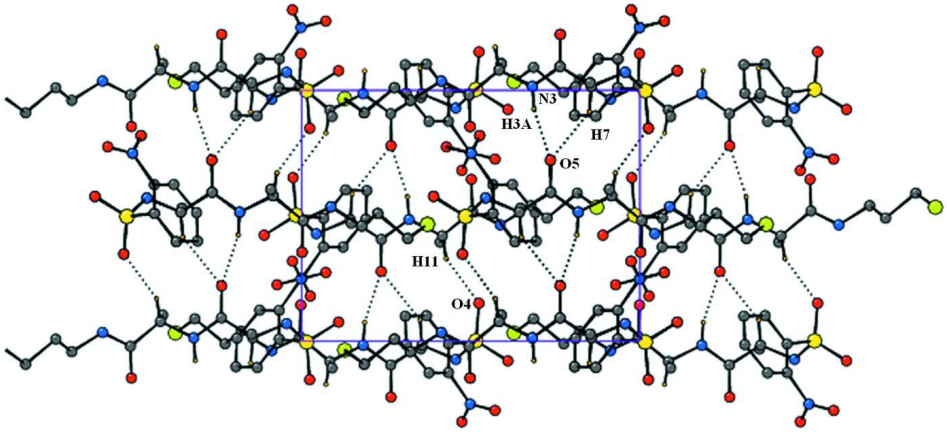


**Figure 2**

Packing diagram of (I). The dotted lines indicate intermolecular C—H···O and N—H···O interactions.

**N-{1-[(3-Bromopropyl)aminocarbonyl]ethyl}-2-(2- nitrobenzenesulfonamido)propionamide**

*Crystal data*

$C_{15}H_{21}BrN_4O_6S$
$M_r = 465.33$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 9.4467$ (4) Å
$b = 12.7438$ (5) Å
$c = 17.3257$ (7) Å
$V = 2085.79$ (15) Å$^3$
$Z = 4$
$F(000) = 948$
$D_x = 1.479$ Mg m$^{-3}$
Melting point: 404 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3007 reflections
$\theta = 2.0$–$26.0°$
$\mu = 2.11$ mm$^{-1}$
$T = 292$ K
Needle, colourless
0.30 × 0.20 × 0.10 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.571$, $T_{max} = 0.817$
33853 measured reflections
4107 independent reflections
3007 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -21 \rightarrow 21$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.138$
$S = 1.10$
4107 reflections
247 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{min} = -0.51$ e Å$^{-3}$
Absolute structure: Flack (1983), 1763 Friedel pairs
Absolute structure parameter: −0.011 (13)

*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.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.53403 (7) | −0.37246 (5) | 1.22175 (4) | 0.0837 (3) |
| S1 | 0.50247 (10) | 0.51539 (8) | 0.93158 (6) | 0.0381 (3) |
| C1 | 0.4914 (5) | 0.4329 (3) | 0.8477 (2) | 0.0399 (9) |

| | | | | |
|---|---|---|---|---|
| C4 | 0.4882 (8) | 0.3109 (5) | 0.7161 (3) | 0.0774 (18) |
| H4 | 0.4882 | 0.2697 | 0.6719 | 0.093* |
| C2 | 0.6041 (5) | 0.3690 (4) | 0.8313 (3) | 0.0553 (12) |
| H2 | 0.6826 | 0.3681 | 0.8637 | 0.066* |
| C6 | 0.3764 (5) | 0.4355 (4) | 0.7986 (3) | 0.0436 (11) |
| C5 | 0.3759 (6) | 0.3765 (4) | 0.7309 (3) | 0.0633 (14) |
| H5 | 0.3009 | 0.3815 | 0.6963 | 0.076* |
| C3 | 0.6009 (6) | 0.3060 (4) | 0.7667 (4) | 0.0692 (16) |
| H3 | 0.6751 | 0.2599 | 0.7571 | 0.083* |
| O3 | 0.4231 (3) | 0.6086 (2) | 0.91578 (19) | 0.0506 (8) |
| O4 | 0.6505 (3) | 0.5244 (3) | 0.9481 (2) | 0.0550 (9) |
| O1 | 0.1799 (4) | 0.4744 (3) | 0.8693 (2) | 0.0690 (10) |
| O2 | 0.2243 (5) | 0.5726 (3) | 0.7713 (3) | 0.0828 (12) |
| N1 | 0.2509 (4) | 0.5005 (4) | 0.8145 (3) | 0.0526 (10) |
| N2 | 0.4295 (3) | 0.4562 (2) | 1.0023 (2) | 0.0345 (8) |
| H2A | 0.3557 | 0.4835 | 1.0233 | 0.041* |
| C9 | 0.4065 (4) | 0.2648 (3) | 0.9969 (3) | 0.0363 (9) |
| C7 | 0.4847 (4) | 0.3563 (3) | 1.0325 (2) | 0.0335 (8) |
| H7 | 0.5856 | 0.3507 | 1.0199 | 0.040* |
| C8 | 0.4666 (7) | 0.3526 (4) | 1.1197 (3) | 0.0709 (16) |
| H8A | 0.5211 | 0.4078 | 1.1430 | 0.106* |
| H8B | 0.4988 | 0.2860 | 1.1388 | 0.106* |
| H8C | 0.3685 | 0.3617 | 1.1325 | 0.106* |
| O5 | 0.2778 (3) | 0.2645 (3) | 0.9909 (2) | 0.0607 (10) |
| N3 | 0.4858 (3) | 0.1824 (2) | 0.9757 (2) | 0.0362 (8) |
| H3A | 0.5765 | 0.1867 | 0.9789 | 0.043* |
| C12 | 0.5198 (4) | −0.0043 (3) | 0.9661 (2) | 0.0383 (9) |
| C10 | 0.4212 (4) | 0.0847 (3) | 0.9472 (3) | 0.0432 (11) |
| H10 | 0.3307 | 0.0735 | 0.9735 | 0.052* |
| C11 | 0.3953 (6) | 0.0907 (4) | 0.8584 (3) | 0.0611 (14) |
| H11A | 0.3342 | 0.1489 | 0.8471 | 0.092* |
| H11B | 0.3518 | 0.0268 | 0.8411 | 0.092* |
| H11C | 0.4841 | 0.1001 | 0.8323 | 0.092* |
| O6 | 0.6452 (3) | −0.0016 (2) | 0.94723 (19) | 0.0473 (8) |
| N4 | 0.4607 (4) | −0.0872 (3) | 1.0009 (2) | 0.0497 (9) |
| H4A | 0.3710 | −0.0865 | 1.0092 | 0.060* |
| C13 | 0.5414 (6) | −0.1783 (4) | 1.0252 (3) | 0.0582 (13) |
| H13A | 0.6400 | −0.1582 | 1.0307 | 0.070* |
| H13B | 0.5362 | −0.2312 | 0.9851 | 0.070* |
| C14 | 0.4926 (6) | −0.2250 (4) | 1.0989 (3) | 0.0663 (14) |
| H14A | 0.3973 | −0.2521 | 1.0924 | 0.080* |
| H14B | 0.4901 | −0.1712 | 1.1385 | 0.080* |
| C15 | 0.5908 (7) | −0.3138 (5) | 1.1244 (3) | 0.0698 (15) |
| H15A | 0.6866 | −0.2872 | 1.1287 | 0.084* |
| H15B | 0.5905 | −0.3686 | 1.0855 | 0.084* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0935 (5) | 0.0790 (5) | 0.0787 (4) | −0.0189 (3) | −0.0056 (3) | 0.0102 (4) |
| S1 | 0.0347 (5) | 0.0326 (5) | 0.0469 (6) | −0.0058 (4) | −0.0054 (4) | 0.0037 (4) |
| C1 | 0.042 (2) | 0.037 (2) | 0.041 (2) | 0.0002 (19) | 0.0050 (19) | 0.0055 (18) |
| C4 | 0.111 (5) | 0.065 (3) | 0.056 (3) | −0.004 (4) | 0.031 (4) | −0.018 (3) |
| C2 | 0.049 (3) | 0.053 (3) | 0.064 (3) | 0.003 (2) | 0.013 (2) | 0.002 (3) |
| C6 | 0.048 (3) | 0.043 (3) | 0.039 (3) | −0.006 (2) | 0.0000 (18) | −0.004 (2) |
| C5 | 0.075 (4) | 0.066 (3) | 0.049 (3) | −0.011 (3) | 0.003 (2) | −0.003 (3) |
| C3 | 0.071 (3) | 0.054 (3) | 0.083 (4) | 0.011 (3) | 0.026 (3) | −0.006 (3) |
| O3 | 0.060 (2) | 0.0286 (15) | 0.063 (2) | 0.0015 (14) | −0.0122 (15) | 0.0029 (15) |
| O4 | 0.0340 (15) | 0.062 (2) | 0.069 (2) | −0.0152 (15) | −0.0057 (14) | 0.0093 (18) |
| O1 | 0.058 (2) | 0.087 (3) | 0.062 (2) | 0.013 (2) | 0.0060 (19) | −0.007 (2) |
| O2 | 0.097 (3) | 0.073 (3) | 0.078 (3) | 0.020 (2) | −0.024 (2) | 0.021 (3) |
| N1 | 0.052 (2) | 0.059 (3) | 0.047 (2) | 0.0065 (19) | −0.0159 (19) | −0.008 (2) |
| N2 | 0.0293 (17) | 0.0308 (17) | 0.043 (2) | −0.0017 (13) | 0.0021 (14) | −0.0028 (15) |
| C9 | 0.029 (2) | 0.030 (2) | 0.050 (3) | −0.0036 (16) | 0.0025 (18) | 0.0012 (19) |
| C7 | 0.0304 (19) | 0.0297 (19) | 0.040 (2) | 0.0039 (16) | −0.0006 (17) | −0.0001 (17) |
| C8 | 0.106 (5) | 0.059 (3) | 0.047 (3) | 0.002 (3) | −0.004 (3) | 0.000 (2) |
| O5 | 0.0262 (15) | 0.0428 (19) | 0.113 (3) | 0.0017 (13) | 0.0000 (17) | −0.021 (2) |
| N3 | 0.0216 (15) | 0.0293 (16) | 0.058 (2) | −0.0037 (14) | −0.0016 (15) | −0.0067 (15) |
| C12 | 0.034 (2) | 0.032 (2) | 0.050 (2) | −0.0031 (17) | −0.0015 (17) | −0.0110 (18) |
| C10 | 0.030 (2) | 0.029 (2) | 0.070 (3) | −0.0064 (16) | 0.003 (2) | −0.006 (2) |
| C11 | 0.075 (4) | 0.049 (3) | 0.059 (3) | 0.000 (2) | −0.023 (3) | −0.011 (3) |
| O6 | 0.0345 (15) | 0.0413 (17) | 0.066 (2) | −0.0021 (13) | 0.0056 (13) | −0.0032 (16) |
| N4 | 0.041 (2) | 0.040 (2) | 0.068 (2) | −0.0050 (16) | 0.0005 (17) | 0.0037 (18) |
| C13 | 0.063 (3) | 0.038 (2) | 0.074 (4) | 0.001 (2) | 0.003 (3) | −0.001 (2) |
| C14 | 0.062 (3) | 0.052 (3) | 0.086 (4) | −0.009 (3) | 0.001 (3) | 0.001 (3) |
| C15 | 0.089 (4) | 0.068 (4) | 0.053 (3) | −0.002 (3) | −0.004 (3) | −0.002 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C15 | 1.921 (6) | C7—H7 | 0.9800 |
| S1—O3 | 1.431 (3) | C8—H8A | 0.9600 |
| S1—O4 | 1.431 (3) | C8—H8B | 0.9600 |
| S1—N2 | 1.595 (3) | C8—H8C | 0.9600 |
| S1—C1 | 1.797 (4) | N3—C10 | 1.471 (5) |
| C1—C2 | 1.370 (7) | N3—H3A | 0.8600 |
| C1—C6 | 1.380 (6) | C12—O6 | 1.229 (5) |
| C4—C5 | 1.375 (8) | C12—N4 | 1.338 (5) |
| C4—C3 | 1.381 (9) | C12—C10 | 1.503 (6) |
| C4—H4 | 0.9300 | C10—C11 | 1.560 (6) |
| C2—C3 | 1.377 (7) | C10—H10 | 0.9800 |
| C2—H2 | 0.9300 | C11—H11A | 0.9600 |
| C6—C5 | 1.393 (7) | C11—H11B | 0.9600 |
| C6—N1 | 1.473 (6) | C11—H11C | 0.9600 |
| C5—H5 | 0.9300 | N4—C13 | 1.452 (6) |

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|---|---|---|---|
| C3—H3 | 0.9300 | N4—H4A | 0.8600 |
| O1—N1 | 1.209 (6) | C13—C14 | 1.482 (8) |
| O2—N1 | 1.211 (6) | C13—H13A | 0.9700 |
| N2—C7 | 1.472 (5) | C13—H13B | 0.9700 |
| N2—H2A | 0.8600 | C14—C15 | 1.529 (8) |
| C9—O5 | 1.220 (5) | C14—H14A | 0.9700 |
| C9—N3 | 1.342 (5) | C14—H14B | 0.9700 |
| C9—C7 | 1.513 (5) | C15—H15A | 0.9700 |
| C7—C8 | 1.521 (6) | C15—H15B | 0.9700 |

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|---|---|---|---|
| O3—S1—O4 | 118.90 (19) | C7—C8—H8C | 109.5 |
| O3—S1—N2 | 108.22 (19) | H8A—C8—H8C | 109.5 |
| O4—S1—N2 | 107.87 (19) | H8B—C8—H8C | 109.5 |
| O3—S1—C1 | 107.47 (19) | C9—N3—C10 | 121.5 (3) |
| O4—S1—C1 | 105.4 (2) | C9—N3—H3A | 119.3 |
| N2—S1—C1 | 108.64 (18) | C10—N3—H3A | 119.3 |
| C2—C1—C6 | 119.8 (4) | O6—C12—N4 | 122.9 (4) |
| C2—C1—S1 | 118.1 (4) | O6—C12—C10 | 121.2 (4) |
| C6—C1—S1 | 122.0 (3) | N4—C12—C10 | 115.8 (3) |
| C5—C4—C3 | 120.3 (5) | N3—C10—C12 | 108.0 (3) |
| C5—C4—H4 | 119.8 | N3—C10—C11 | 110.8 (4) |
| C3—C4—H4 | 119.8 | C12—C10—C11 | 110.4 (4) |
| C1—C2—C3 | 119.9 (5) | N3—C10—H10 | 109.2 |
| C1—C2—H2 | 120.1 | C12—C10—H10 | 109.2 |
| C3—C2—H2 | 120.1 | C11—C10—H10 | 109.2 |
| C1—C6—C5 | 120.6 (5) | C10—C11—H11A | 109.5 |
| C1—C6—N1 | 122.1 (4) | C10—C11—H11B | 109.5 |
| C5—C6—N1 | 117.3 (4) | H11A—C11—H11B | 109.5 |
| C4—C5—C6 | 118.8 (5) | C10—C11—H11C | 109.5 |
| C4—C5—H5 | 120.6 | H11A—C11—H11C | 109.5 |
| C6—C5—H5 | 120.6 | H11B—C11—H11C | 109.5 |
| C2—C3—C4 | 120.4 (5) | C12—N4—C13 | 122.9 (4) |
| C2—C3—H3 | 119.8 | C12—N4—H4A | 118.6 |
| C4—C3—H3 | 119.8 | C13—N4—H4A | 118.6 |
| O1—N1—O2 | 125.4 (5) | N4—C13—C14 | 114.1 (5) |
| O1—N1—C6 | 116.0 (4) | N4—C13—H13A | 108.7 |
| O2—N1—C6 | 118.6 (4) | C14—C13—H13A | 108.7 |
| C7—N2—S1 | 122.0 (3) | N4—C13—H13B | 108.7 |
| C7—N2—H2A | 119.0 | C14—C13—H13B | 108.7 |
| S1—N2—H2A | 119.0 | H13A—C13—H13B | 107.6 |
| O5—C9—N3 | 122.1 (4) | C13—C14—C15 | 111.0 (5) |
| O5—C9—C7 | 121.6 (4) | C13—C14—H14A | 109.4 |
| N3—C9—C7 | 116.3 (3) | C15—C14—H14A | 109.4 |
| N2—C7—C9 | 110.4 (3) | C13—C14—H14B | 109.4 |
| N2—C7—C8 | 109.9 (4) | C15—C14—H14B | 109.4 |
| C9—C7—C8 | 109.0 (4) | H14A—C14—H14B | 108.0 |
| N2—C7—H7 | 109.2 | C14—C15—Br1 | 111.9 (4) |
| C9—C7—H7 | 109.2 | C14—C15—H15A | 109.2 |

| | | | |
|---|---|---|---|
| C8—C7—H7 | 109.2 | Br1—C15—H15A | 109.2 |
| C7—C8—H8A | 109.5 | C14—C15—H15B | 109.2 |
| C7—C8—H8B | 109.5 | Br1—C15—H15B | 109.2 |
| H8A—C8—H8B | 109.5 | H15A—C15—H15B | 107.9 |
| | | | |
| O3—S1—C1—C2 | 148.8 (4) | O4—S1—N2—C7 | −50.8 (3) |
| O4—S1—C1—C2 | 21.1 (4) | C1—S1—N2—C7 | 62.9 (3) |
| N2—S1—C1—C2 | −94.3 (4) | S1—N2—C7—C9 | −95.6 (4) |
| O3—S1—C1—C6 | −28.7 (4) | S1—N2—C7—C8 | 144.0 (4) |
| O4—S1—C1—C6 | −156.4 (4) | O5—C9—C7—N2 | −45.2 (5) |
| N2—S1—C1—C6 | 88.2 (4) | N3—C9—C7—N2 | 137.9 (4) |
| C6—C1—C2—C3 | −1.3 (7) | O5—C9—C7—C8 | 75.7 (6) |
| S1—C1—C2—C3 | −178.8 (4) | N3—C9—C7—C8 | −101.3 (5) |
| C2—C1—C6—C5 | −2.4 (7) | O5—C9—N3—C10 | −2.8 (7) |
| S1—C1—C6—C5 | 175.0 (4) | C7—C9—N3—C10 | 174.1 (4) |
| C2—C1—C6—N1 | 178.3 (4) | C9—N3—C10—C12 | −152.0 (4) |
| S1—C1—C6—N1 | −4.3 (6) | C9—N3—C10—C11 | 87.0 (5) |
| C3—C4—C5—C6 | −1.7 (8) | O6—C12—C10—N3 | −52.6 (5) |
| C1—C6—C5—C4 | 3.9 (7) | N4—C12—C10—N3 | 130.4 (4) |
| N1—C6—C5—C4 | −176.8 (5) | O6—C12—C10—C11 | 68.6 (5) |
| C1—C2—C3—C4 | 3.5 (8) | N4—C12—C10—C11 | −108.4 (4) |
| C5—C4—C3—C2 | −1.9 (9) | O6—C12—N4—C13 | 5.1 (7) |
| C1—C6—N1—O1 | −67.9 (6) | C10—C12—N4—C13 | −178.0 (4) |
| C5—C6—N1—O1 | 112.8 (5) | C12—N4—C13—C14 | 143.2 (5) |
| C1—C6—N1—O2 | 114.4 (5) | N4—C13—C14—C15 | −174.7 (4) |
| C5—C6—N1—O2 | −64.9 (6) | C13—C14—C15—Br1 | 177.8 (4) |
| O3—S1—N2—C7 | 179.3 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2*A*···O6$^{i}$ | 0.86 | 2.07 | 2.884 (4) | 158 |
| N3—H3*A*···O6 | 0.86 | 2.54 | 2.829 (4) | 100 |
| N3—H3*A*···O5$^{ii}$ | 0.86 | 2.07 | 2.899 (4) | 162 |
| N4—H4*A*···O4$^{i}$ | 0.86 | 2.35 | 3.165 (5) | 159 |
| C2—H2···O4 | 0.93 | 2.49 | 2.867 (6) | 104 |
| C7—H7···O5$^{ii}$ | 0.98 | 2.34 | 3.193 (5) | 145 |
| C10—H10···O4$^{i}$ | 0.98 | 2.51 | 3.431 (5) | 156 |
| C13—H13*A*···O6 | 0.97 | 2.46 | 2.802 (6) | 100 |
| C13—H13*B*···O3$^{iii}$ | 0.97 | 2.60 | 3.496 (6) | 154 |
| C11—H11*A*···*Cg* | 3.39 | 0.96 | 3.922 (6) | 117 |
| C11—H11*B*···*Cg*$^{i}$ | 3.27 | 0.96 | 3.857 (6) | 121 |

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