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

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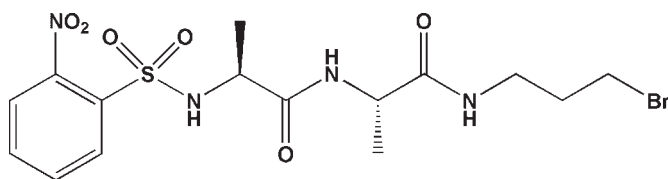
Received 24 July 2009; accepted 27 August 2009

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

In the title compound, $\text{C}_{15}\text{H}_{21}\text{BrN}_4\text{O}_6\text{S}$, all three NH groups are involved in intermolecular $\text{N}-\text{H}\cdots\text{O}$ interactions which, together with two intermolecular $\text{C}-\text{H}\cdots\text{O}$ contacts, lead to a continuous antiparallel β -sheet structure. There are no $\pi-\pi$ interactions between molecules, and two $\text{C}-\text{H}\cdots\pi$ interactions primarily govern the linkage between sheets.

Related literature

For conformationally restricted peptide analogues, see: Belvisi *et al.* (2000); Ripka *et al.* (1993). For $\text{C}-\text{H}\cdots\pi$ 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 β -strand structures, see: Loughlin *et al.* (2004).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{21}\text{BrN}_4\text{O}_6\text{S}$

$M_r = 465.33$

Orthorhombic, $P2_12_12_1$

$a = 9.4467$ (4) Å

$b = 12.7438$ (5) Å

$c = 17.3257$ (7) Å

$V = 2085.79$ (15) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 2.11$ mm⁻¹

$T = 292$ K

$0.30 \times 0.20 \times 0.10$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

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

$\Delta\rho_{\text{max}} = 0.50$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Absolute structure: Flack (1983),

1763 Friedel pairs

Flack parameter: -0.011 (13)

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{N}2-\text{H}2\text{A}\cdots\text{O}6^i$ | 0.86 | 2.07 | 2.884 (4) | 158 |
| $\text{N}3-\text{H}3\text{A}\cdots\text{O}6$ | 0.86 | 2.54 | 2.829 (4) | 100 |
| $\text{N}3-\text{H}3\text{A}\cdots\text{O}5^{\text{ii}}$ | 0.86 | 2.07 | 2.899 (4) | 162 |
| $\text{N}4-\text{H}4\text{A}\cdots\text{O}4^i$ | 0.86 | 2.35 | 3.165 (5) | 159 |
| $\text{C}2-\text{H}2\cdots\text{O}4$ | 0.93 | 2.49 | 2.867 (6) | 104 |
| $\text{C}7-\text{H}7\cdots\text{O}5^{\text{ii}}$ | 0.98 | 2.34 | 3.193 (5) | 145 |
| $\text{C}10-\text{H}10\cdots\text{O}4^i$ | 0.98 | 2.51 | 3.431 (5) | 156 |
| $\text{C}13-\text{H}13\text{A}\cdots\text{O}6$ | 0.97 | 2.46 | 2.802 (6) | 100 |
| $\text{C}13-\text{H}13\text{B}\cdots\text{O}3^{\text{iii}}$ | 0.97 | 2.60 | 3.496 (6) | 154 |
| $\text{C}11-\text{H}11\text{A}\cdots\text{C}g$ | 3.39 | 0.96 | 3.922 (6) | 117 |
| $\text{C}11-\text{H}11\text{B}\cdots\text{C}g^i$ | 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) $x, y - 1, z$. $\text{C}g$ is the centroid of the $\text{C}1-\text{C}6$ 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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N-{1-[(3-Bromopropyl)aminocarbonyl]ethyl}-2-(2-nitrobenzenesulfonamido)propionamide

R. Thirupathi, D. N. Reddy, S. Brinda and E. N. Prabhakaran

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, N₃—H₃ and N₄—H₄, 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 β -strand structures (Loughlin *et al.*, 2004). On the other hand, the two adjacent N-H bonds N₂—H₂ and N₃—H₃ 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 β -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 β -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··· π interactions. One is intermolecular (C₁₁—C_g = 3.85 Å, C_g: the centroid of the phenyl ring) and the other is intramolecular (C₁₁—C_g = 3.92 Å). There are no π — π interactions between the phenyl rings and the interactions between the sheets are solely governed by the C—H··· π interactions.

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 morpholine (0.31 ml, 2.82 mmol) followed by ethylchloroformate (0.18 ml, 1.93 mmol) under N₂ atmosphere. After two minutes a solution of 3-bromopropan-1-ammonium bromide (536 mg, 2.44 mmol) and *N*-Methyl morpholine (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 NaHCO₃ (5 ml) solution and dried (anhydrous Na₂SO₄). 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

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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 mM).

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 $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms.

Figures

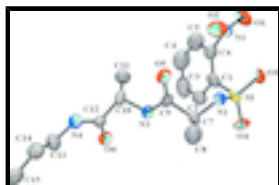


Fig. 1. View of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity.

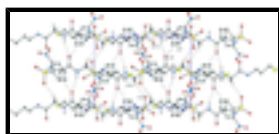


Fig. 2. Packing diagram of (I). The dotted lines indicate intermolecular C—H...O and N—H...O interactions.

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

Crystal data

$\text{C}_{15}\text{H}_{21}\text{BrN}_4\text{O}_6\text{S}$

$M_r = 465.33$

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) Å³

$Z = 4$

$F(000) = 948$

$D_x = 1.479$ 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

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)

$T_{\text{min}} = 0.571$, $T_{\text{max}} = 0.817$

33853 measured reflections

4107 independent reflections

3007 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.054$

$\theta_{\text{max}} = 26.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$

$h = -11 \rightarrow 11$

$k = -15 \rightarrow 15$

$l = -21 \rightarrow 21$

Refinement

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| 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) |

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| | | | | |
|------|------------|-------------|--------------|-------------|
| 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 (\AA^2)

| | 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, °)

| | | | |
|----------|-------------|------------|-----------|
| 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) |
| 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 |
| 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) |

supplementary materials

| | | | |
|-------------|------------|----------------|------------|
| 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 (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N2—H2A \cdots O6 ⁱ | 0.86 | 2.07 | 2.884 (4) | 158 |
| N3—H3A \cdots O6 | 0.86 | 2.54 | 2.829 (4) | 100 |
| N3—H3A \cdots O5 ⁱⁱ | 0.86 | 2.07 | 2.899 (4) | 162 |
| N4—H4A \cdots O4 ⁱ | 0.86 | 2.35 | 3.165 (5) | 159 |
| C2—H2 \cdots O4 | 0.93 | 2.49 | 2.867 (6) | 104 |
| C7—H7 \cdots O5 ⁱⁱ | 0.98 | 2.34 | 3.193 (5) | 145 |
| C10—H10 \cdots O4 ⁱ | 0.98 | 2.51 | 3.431 (5) | 156 |
| C13—H13A \cdots O6 | 0.97 | 2.46 | 2.802 (6) | 100 |
| C13—H13B \cdots O3 ⁱⁱⁱ | 0.97 | 2.60 | 3.496 (6) | 154 |
| C11—H11A \cdots Cg | 3.39 | 0.96 | 3.922 (6) | 117 |
| C11—H11B \cdots 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) $x, y-1, z$.

Fig. 1

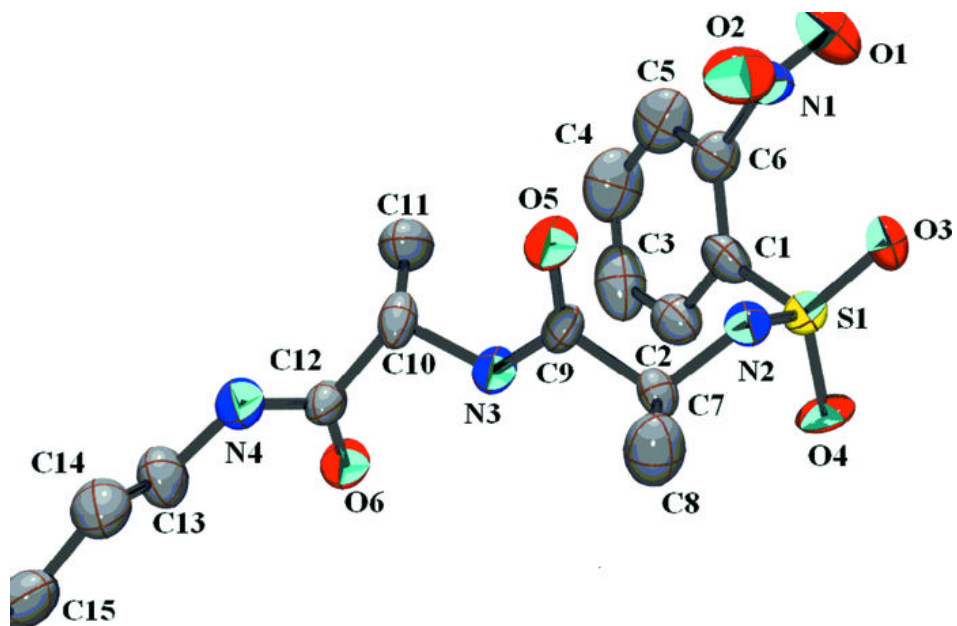


Fig. 2

