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# Crystal structure of diethylammonium aniline-4-sulfonate anilinium-4-sulfonate

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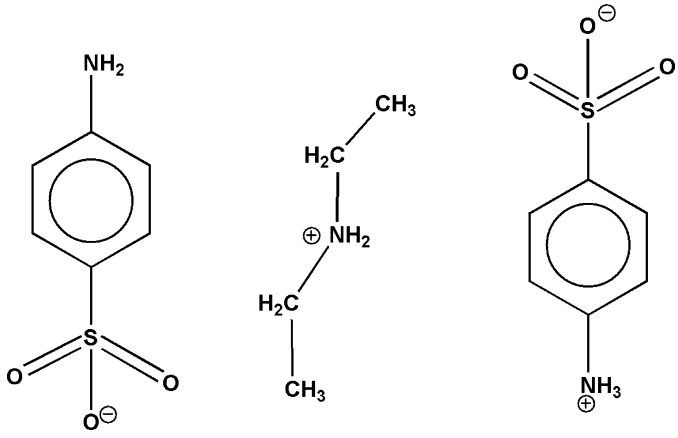
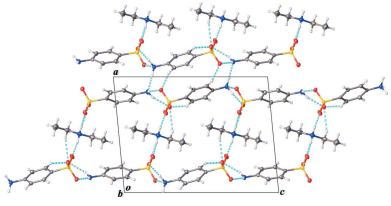
The title compound, $C_4H_{12}N^+\cdot C_6H_6NO_3S^-\cdot C_6H_7NO_3S$, consists of an ion pair and a zwitterionic neutral molecule. The cation adopts an extended conformation [C—C—N—C torsion angles = 177.1 (3) and −178.4 (3)°]. In the crystal, the components are linked by N—H···O and N—H···N hydrogen bonds, generating a three-dimensional network, which is consolidated by weak C—H···O interactions.

## 1. Chemical context

Acids such as sulfuric, nitric, oxalic, phosphoric, substituted sulfonic, etc. when mixed in water with amines give acidic or neutral salts that may be soluble in organic solvents: this solubility allows for the study of their interactions with metal halides, acetates, nitrates, perchlorates, *etc*, which yield new adducts and complexes in which the conjugate anion of the acid behaves as a ligand, usually coordinating the metal ion (Najafi *et al.*, 2011*a*,*b*; Ittyachan *et al.*, 2016; Majeed & Wendt, 2016).





We report here the synthesis and structure of the product arising from the mixing of diethylamine and anilinesulfonic acid solutions, which contains a combination of ions and a zwitterion. In terms of other compounds containing both the anilinesulfonate anion and its zwitterionic form, anilinium-sulfonate, to date only the 4-aminopyridinium salt has been reported (Fun *et al.*, 2008).

## 2. Structural commentary

There is one diethylammonium cation, one anilinesulfonate anion and one zwitterionic aniliniumsulfonate molecule in the

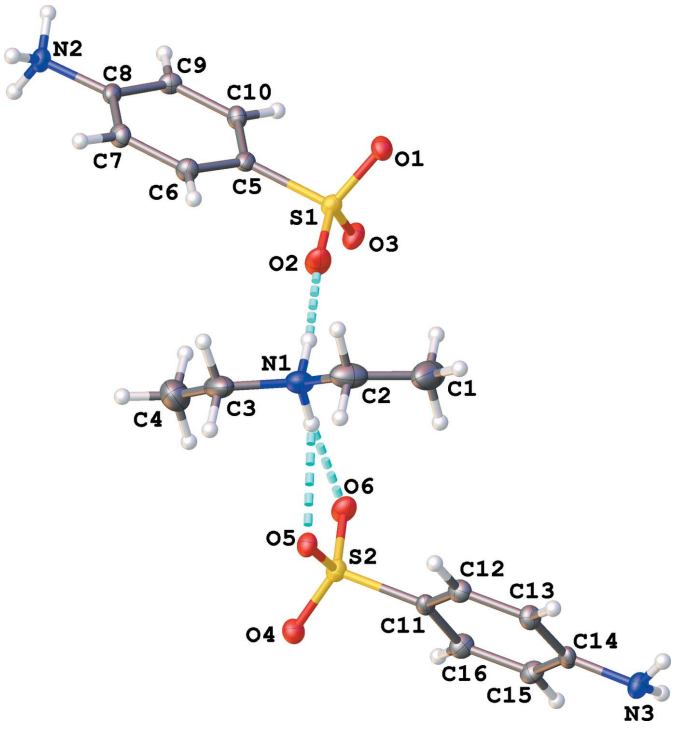



**Figure 1**
The molecular structure of the title compound. Displacement ellipsoids depicted at the 50% probability level and H atoms as spheres of an arbitrary radius. Hydrogen bonds are represented by light-blue dashed lines.

asymmetric unit (Fig. 1). The individual molecules are unremarkable with bond distances and angles typical of their type. The cation adopts an extended conformation [C1—C2—N1—C3 and C2—N1—C3—C4 torsion angles = 177.1 (3) and −178.4 (3)°, respectively].

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1*NA*···O2 | 0.96 (3) | 1.79 (4) | 2.748 (4) | 175 (3) |
| N1—H1*NB*···O5 | 0.90 (3) | 2.45 (3) | 3.019 (4) | 122 (3) |
| N1—H1*NB*···O6 | 0.90 (3) | 2.03 (4) | 2.920 (4) | 173 (3) |
| N2—H2*NA*···O4$^{i}$ | 0.94 (2) | 1.88 (2) | 2.794 (4) | 165 (3) |
| N2—H2*NB*···O5$^{ii}$ | 0.94 (2) | 1.85 (2) | 2.778 (3) | 171 (3) |
| N2—H2*NC*···N3$^{iii}$ | 0.97 (2) | 1.85 (2) | 2.812 (4) | 178 (4) |
| N3—H3*NA*···O1$^{iv}$ | 0.83 (4) | 2.21 (4) | 2.998 (4) | 157 (3) |
| N3—H3*NB*···O3$^{v}$ | 0.79 (3) | 2.23 (3) | 2.997 (4) | 164 (3) |
| C3—H3*A*···O3$^{vi}$ | 0.99 | 2.48 | 3.338 (4) | 145 |
| C6—H6···O3$^{vi}$ | 0.95 | 2.65 | 3.507 (4) | 151 |
| C9—H9···O1$^{vii}$ | 0.95 | 2.59 | 3.517 (4) | 165 |

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+1$; (ii) $-x+1, y+\frac{1}{2}, -z+1$; (iii) $x-1, y, z-1$; (iv) $-x+1, y+\frac{1}{2}, -z+2$; (v) $-x+1, y-\frac{1}{2}, -z+2$; (vi) $x, y-1, z$; (vii) $-x, y+\frac{1}{2}, -z+1$.

## 3. Supramolecular features

The zwitterionic aniliniumsulfonate and the anilinesulfonate anion are connected through N2—H2*NA*···O4$^{i}$, N2—H2*NB*···O5$^{ii}$, N2—H2*NC*···N3$^{iii}$, N3—H3*NA*···O1$^{iv}$ and N3—H3*NB*···O3$^{v}$ hydrogen bonds (Table 1) giving sheet-like bi-layers that lie parallel to the *bc* plane [symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+1$; (ii) $-x+1, y+\frac{1}{2}, -z+1$; (iii) $x-1, y, z-1$; (iv) $-x+1, y+\frac{1}{2}, -z+2$; (v) $-x+1, y-\frac{1}{2}, -z+2$]. The bi-layers are then linked through N1—H1*NA*···O2, N1—H1*NB*···O5 and N1—H1*NB*···O6 hydrogen bonds, yielding a three-dimensional network (Fig. 2). Some weak C—H···O (C3—H3*A*···O3$^{vi}$, C6—H6···O3$^{vi}$ and C9—H9···O1$^{vii}$) interactions consolidate the packing in the crystal [symmetry codes: (vi) $x, y-1, z$; (vii) $-x, y+\frac{1}{2}, -z+1$]. Examination of the packing reveals layers of diethyl ammonium cation sandwiched between bi-layers of aniline sulfate moieties. The key

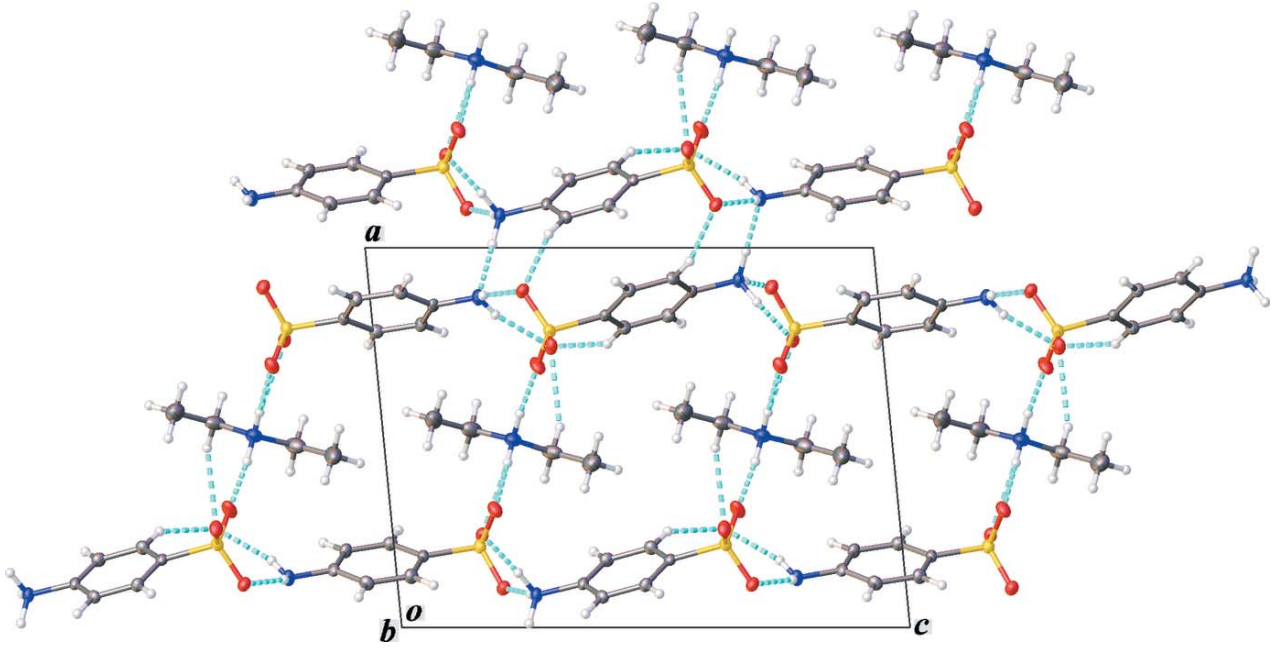



**Figure 2**
Packing diagram, viewed along the *b* axis. Hydrogen bonds are represented by light-blue dashed lines.

hydrogen bonds establishing the three-dimensional array are the contacts to sulfonate oxygen atoms and the N2···N3 aniline interactions. All amine hydrogen atoms form good hydrogen-bond contacts to neighboring hydrogen-bond acceptor atoms.

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.37 + one update; Groom *et al.*, 2016) shows 46 hits concerning the anilinesulfonate anion, three containing aniliniumsulfonate and one hit with both (Fun *et al.*, 2008), while 303 hits concern the diethylammonium ion.

## 5. Synthesis and crystallization

Dimethyl amine was mixed in water with aniline sulfonic acid in a 1:1 ratio. Colorless block-like crystals were obtained on allowing the water to evaporate at 333 K.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bonded to carbon were included in geometrically calculated positions and allowed to ride on the parent atom. All amine hydrogen atoms were located in a difference Fourier map and refined freely.

As the molecules are achiral, only the correct enantiomorph of the space group was determined: this was determined by comparison of intensities of Friedel pairs of reflections yielding a Flack *x* parameter of 0.03 (6) (Parsons *et al.*, 2013) and a Hooft *y* parameter of 0.04 (6) (Hooft *et al.*, 2008).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_4H_{12}N^+\cdot C_6H_6NO_3S^-\cdot C_6H_7NO_3S$ |
| $M_r$ | 419.51 |
| Crystal system, space group | Monoclinic, $P2_1$ |
| Temperature (K) | 120 |
| $a, b, c$ (Å) | 11.419 (3), 5.6731 (16), 15.226 (4) |
| $\beta$ (°) | 95.530 (4) |
| $V$ (Å$^3$) | 981.8 (5) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.31 |
| Crystal size (mm) | 0.22 × 0.19 × 0.05 |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Krause *et al.*, 2015) |
| $T_{min}$, $T_{max}$ | 0.781, 0.931 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 18906, 4911, 4228 |
| $R_{int}$ | 0.056 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.668 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.039, 0.077, 0.98 |
| No. of reflections | 4911 |
| No. of parameters | 274 |
| No. of restraints | 4 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.29, −0.38 |
| Absolute structure | Flack *x* determined using 1632 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | 0.03 (6) |

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

## Acknowledgements

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# supporting information

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## Crystal structure of diethylammonium aniline-4-sulfonate anilinium-4-sulfonate

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### Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Diethylammonium aniline-4-sulfonate anilinium-4-sulfonate

*Crystal data*

$C_4H_{12}N^+·C_6H_6NO_3S^-·C_6H_7NO_3S$
$M_r$ = 419.51
Monoclinic, $P2_1$
$a$ = 11.419 (3) Å
$b$ = 5.6731 (16) Å
$c$ = 15.226 (4) Å
$\beta$ = 95.530 (4)°
$V$ = 981.8 (5) Å$^3$
$Z$ = 2
$F(000)$ = 444
$D_x$ = 1.419 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 4341 reflections
$\theta$ = 2.7–24.5°
$\mu$ = 0.31 mm$^{-1}$
$T$ = 120 K
Plate, colorless
0.22 × 0.19 × 0.05 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.33 pixels mm$^{-1}$
combination of $\omega$ and $\varphi$–scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min}$ = 0.781, $T_{max}$ = 0.931
18906 measured reflections
4911 independent reflections
4228 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.056
$\theta_{max}$ = 28.4°, $\theta_{min}$ = 1.3°
$h$ = −15→15
$k$ = −7→7
$l$ = −20→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.077
$S$ = 0.98
4911 reflections
274 parameters
4 restraints
Primary atom site location: real-space vector search
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 1632 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.03 (6)

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| N1 | 0.5053 (3) | 0.0636 (5) | 0.74539 (18) | 0.0247 (7) |
| H1NA | 0.437 (3) | 0.156 (6) | 0.727 (2) | 0.033 (10)* |
| H1NB | 0.566 (3) | 0.160 (6) | 0.761 (2) | 0.031 (11)* |
| C1 | 0.4529 (3) | 0.0950 (8) | 0.8976 (2) | 0.0461 (11) |
| H1A | 0.4323 | 0.0039 | 0.9486 | 0.069* |
| H1B | 0.3869 | 0.1973 | 0.8767 | 0.069* |
| H1C | 0.5224 | 0.1918 | 0.9148 | 0.069* |
| C2 | 0.4791 (3) | −0.0698 (7) | 0.8253 (2) | 0.0365 (10) |
| H2A | 0.5474 | −0.1696 | 0.8458 | 0.044* |
| H2B | 0.4106 | −0.1743 | 0.8104 | 0.044* |
| C3 | 0.5386 (3) | −0.0861 (7) | 0.6708 (2) | 0.0336 (9) |
| H3A | 0.4730 | −0.1938 | 0.6512 | 0.040* |
| H3B | 0.6083 | −0.1829 | 0.6907 | 0.040* |
| C4 | 0.5661 (3) | 0.0694 (8) | 0.5950 (2) | 0.0459 (11) |
| H4A | 0.5848 | −0.0291 | 0.5453 | 0.069* |
| H4B | 0.6337 | 0.1699 | 0.6138 | 0.069* |
| H4C | 0.4977 | 0.1683 | 0.5767 | 0.069* |
| S1 | 0.21877 (6) | 0.48653 (13) | 0.65278 (5) | 0.01702 (18) |
| O1 | 0.11341 (17) | 0.4576 (4) | 0.69828 (12) | 0.0192 (5) |
| O2 | 0.3108 (2) | 0.3205 (4) | 0.68312 (15) | 0.0281 (6) |
| O3 | 0.25973 (19) | 0.7296 (4) | 0.65346 (13) | 0.0221 (5) |
| N2 | 0.0854 (2) | 0.2713 (5) | 0.27136 (16) | 0.0166 (6) |
| H2NA | 0.088 (3) | 0.109 (4) | 0.2598 (18) | 0.017 (8)* |
| H2NB | 0.144 (2) | 0.338 (6) | 0.239 (2) | 0.027 (10)* |
| H2NC | 0.010 (2) | 0.341 (7) | 0.252 (2) | 0.051 (12)* |
| C5 | 0.1782 (3) | 0.4162 (6) | 0.54039 (19) | 0.0152 (7) |
| C6 | 0.2099 (3) | 0.2003 (5) | 0.50528 (19) | 0.0180 (7) |
| H6 | 0.2527 | 0.0874 | 0.5416 | 0.022* |
| C7 | 0.1781 (3) | 0.1530 (6) | 0.41663 (19) | 0.0181 (7) |
| H7 | 0.1995 | 0.0075 | 0.3917 | 0.022* |
| C8 | 0.1153 (3) | 0.3183 (5) | 0.36490 (19) | 0.0149 (7) |
| C9 | 0.0805 (3) | 0.5306 (5) | 0.39992 (19) | 0.0162 (6) |
| H9 | 0.0359 | 0.6415 | 0.3639 | 0.019* |
| C10 | 0.1122 (3) | 0.5774 (5) | 0.48805 (19) | 0.0161 (7) |
| H10 | 0.0886 | 0.7213 | 0.5130 | 0.019* |
| S2 | 0.78723 (7) | 0.26125 (13) | 0.83062 (5) | 0.01669 (18) |
| O4 | 0.89636 (19) | 0.3121 (4) | 0.79229 (13) | 0.0194 (5) |
| O5 | 0.75682 (17) | 0.0109 (4) | 0.82423 (12) | 0.0173 (5) |
| O6 | 0.68960 (19) | 0.4094 (4) | 0.79409 (14) | 0.0231 (5) |

| | | | | |
|---|---|---|---|---|
| N3 | 0.8696 (3) | 0.4851 (6) | 1.21318 (17) | 0.0194 (6) |
| H3NA | 0.874 (3) | 0.630 (7) | 1.223 (2) | 0.028 (11)* |
| H3NB | 0.824 (3) | 0.430 (6) | 1.244 (2) | 0.020 (10)* |
| C11 | 0.8122 (3) | 0.3252 (5) | 0.94423 (19) | 0.0146 (7) |
| C12 | 0.7796 (3) | 0.1654 (5) | 1.00663 (19) | 0.0181 (7) |
| H12 | 0.7445 | 0.0197 | 0.9881 | 0.022* |
| C13 | 0.7982 (3) | 0.2179 (5) | 1.09560 (18) | 0.0178 (7) |
| H13 | 0.7767 | 0.1071 | 1.1380 | 0.021* |
| C14 | 0.8485 (3) | 0.4330 (5) | 1.12326 (19) | 0.0159 (7) |
| C15 | 0.8832 (3) | 0.5891 (5) | 1.06041 (19) | 0.0190 (7) |
| H15 | 0.9198 | 0.7337 | 1.0787 | 0.023* |
| C16 | 0.8650 (3) | 0.5360 (5) | 0.9717 (2) | 0.0201 (7) |
| H16 | 0.8889 | 0.6444 | 0.9293 | 0.024* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| N1 | 0.0186 (16) | 0.0267 (17) | 0.0282 (16) | 0.0017 (13) | −0.0008 (13) | 0.0020 (13) |
| C1 | 0.033 (2) | 0.077 (3) | 0.029 (2) | −0.013 (2) | 0.0030 (18) | 0.004 (2) |
| C2 | 0.0242 (19) | 0.043 (3) | 0.041 (2) | −0.0057 (18) | −0.0012 (17) | 0.0136 (19) |
| C3 | 0.0192 (19) | 0.039 (2) | 0.042 (2) | 0.0001 (16) | −0.0021 (16) | −0.0131 (18) |
| C4 | 0.034 (2) | 0.068 (3) | 0.036 (2) | 0.005 (2) | 0.0077 (19) | −0.006 (2) |
| S1 | 0.0176 (4) | 0.0183 (4) | 0.0148 (4) | 0.0014 (3) | −0.0006 (3) | −0.0003 (3) |
| O1 | 0.0206 (12) | 0.0203 (13) | 0.0174 (11) | −0.0024 (10) | 0.0057 (9) | −0.0005 (10) |
| O2 | 0.0288 (14) | 0.0326 (15) | 0.0214 (12) | 0.0145 (11) | −0.0059 (10) | −0.0002 (10) |
| O3 | 0.0275 (13) | 0.0213 (13) | 0.0176 (11) | −0.0072 (11) | 0.0022 (9) | −0.0037 (10) |
| N2 | 0.0222 (15) | 0.0139 (14) | 0.0139 (13) | −0.0004 (13) | 0.0023 (11) | −0.0005 (12) |
| C5 | 0.0141 (16) | 0.0172 (17) | 0.0147 (15) | −0.0027 (13) | 0.0027 (12) | 0.0000 (12) |
| C6 | 0.0194 (17) | 0.0157 (16) | 0.0186 (15) | 0.0026 (13) | 0.0008 (13) | 0.0012 (12) |
| C7 | 0.0203 (17) | 0.0145 (15) | 0.0198 (16) | 0.0004 (13) | 0.0030 (14) | −0.0026 (13) |
| C8 | 0.0153 (16) | 0.0178 (17) | 0.0120 (15) | −0.0033 (12) | 0.0029 (12) | −0.0001 (12) |
| C9 | 0.0169 (15) | 0.0143 (16) | 0.0172 (15) | 0.0007 (12) | 0.0000 (12) | 0.0037 (12) |
| C10 | 0.0195 (17) | 0.0131 (15) | 0.0162 (15) | 0.0003 (12) | 0.0037 (13) | −0.0008 (12) |
| S2 | 0.0195 (4) | 0.0154 (4) | 0.0149 (4) | 0.0007 (3) | 0.0008 (3) | −0.0002 (3) |
| O4 | 0.0218 (12) | 0.0188 (13) | 0.0182 (11) | −0.0011 (10) | 0.0047 (9) | 0.0008 (9) |
| O5 | 0.0218 (11) | 0.0144 (11) | 0.0161 (10) | −0.0019 (10) | 0.0027 (9) | −0.0019 (9) |
| O6 | 0.0261 (13) | 0.0218 (13) | 0.0201 (12) | 0.0053 (10) | −0.0037 (10) | −0.0001 (9) |
| N3 | 0.0260 (16) | 0.0171 (15) | 0.0152 (13) | −0.0031 (14) | 0.0023 (12) | −0.0007 (13) |
| C11 | 0.0155 (16) | 0.0155 (17) | 0.0127 (15) | 0.0033 (12) | 0.0011 (12) | 0.0009 (12) |
| C12 | 0.0189 (17) | 0.0142 (15) | 0.0213 (16) | −0.0004 (13) | 0.0020 (13) | −0.0005 (12) |
| C13 | 0.0215 (17) | 0.0162 (16) | 0.0162 (15) | −0.0003 (13) | 0.0037 (13) | 0.0025 (12) |
| C14 | 0.0170 (16) | 0.0167 (17) | 0.0141 (15) | 0.0053 (13) | 0.0022 (12) | −0.0019 (12) |
| C15 | 0.0206 (17) | 0.0144 (16) | 0.0214 (16) | −0.0019 (13) | −0.0009 (14) | −0.0016 (13) |
| C16 | 0.0228 (17) | 0.0183 (18) | 0.0191 (16) | −0.0019 (13) | 0.0019 (13) | 0.0034 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| N1—C2 | 1.488 (4) | C6—C7 | 1.390 (4) |
| N1—C3 | 1.497 (4) | C6—H6 | 0.9500 |
| N1—H1NA | 0.96 (3) | C7—C8 | 1.380 (4) |
| N1—H1NB | 0.90 (3) | C7—H7 | 0.9500 |
| C1—C2 | 1.496 (5) | C8—C9 | 1.390 (4) |
| C1—H1A | 0.9800 | C9—C10 | 1.381 (4) |
| C1—H1B | 0.9800 | C9—H9 | 0.9500 |
| C1—H1C | 0.9800 | C10—H10 | 0.9500 |
| C2—H2A | 0.9900 | S2—O4 | 1.455 (2) |
| C2—H2B | 0.9900 | S2—O6 | 1.462 (2) |
| C3—C4 | 1.510 (5) | S2—O5 | 1.463 (2) |
| C3—H3A | 0.9900 | S2—C11 | 1.763 (3) |
| C3—H3B | 0.9900 | N3—C14 | 1.399 (4) |
| C4—H4A | 0.9800 | N3—H3NA | 0.83 (4) |
| C4—H4B | 0.9800 | N3—H3NB | 0.79 (3) |
| C4—H4C | 0.9800 | C11—C16 | 1.386 (4) |
| S1—O2 | 1.453 (2) | C11—C12 | 1.389 (4) |
| S1—O1 | 1.454 (2) | C12—C13 | 1.383 (4) |
| S1—O3 | 1.456 (2) | C12—H12 | 0.9500 |
| S1—C5 | 1.775 (3) | C13—C14 | 1.397 (4) |
| N2—C8 | 1.457 (4) | C13—H13 | 0.9500 |
| N2—H2NA | 0.94 (2) | C14—C15 | 1.389 (4) |
| N2—H2NB | 0.94 (2) | C15—C16 | 1.380 (4) |
| N2—H2NC | 0.97 (2) | C15—H15 | 0.9500 |
| C5—C10 | 1.387 (4) | C16—H16 | 0.9500 |
| C5—C6 | 1.398 (4) | | |
| | | | |
| C2—N1—C3 | 114.7 (3) | C6—C5—S1 | 120.8 (2) |
| C2—N1—H1NA | 107 (2) | C7—C6—C5 | 119.2 (3) |
| C3—N1—H1NA | 110 (2) | C7—C6—H6 | 120.4 |
| C2—N1—H1NB | 108 (2) | C5—C6—H6 | 120.4 |
| C3—N1—H1NB | 107 (2) | C8—C7—C6 | 119.7 (3) |
| H1NA—N1—H1NB | 109 (3) | C8—C7—H7 | 120.1 |
| C2—C1—H1A | 109.5 | C6—C7—H7 | 120.1 |
| C2—C1—H1B | 109.5 | C7—C8—C9 | 121.4 (3) |
| H1A—C1—H1B | 109.5 | C7—C8—N2 | 119.6 (3) |
| C2—C1—H1C | 109.5 | C9—C8—N2 | 119.0 (3) |
| H1A—C1—H1C | 109.5 | C10—C9—C8 | 118.8 (3) |
| H1B—C1—H1C | 109.5 | C10—C9—H9 | 120.6 |
| N1—C2—C1 | 110.7 (3) | C8—C9—H9 | 120.6 |
| N1—C2—H2A | 109.5 | C9—C10—C5 | 120.5 (3) |
| C1—C2—H2A | 109.5 | C9—C10—H10 | 119.7 |
| N1—C2—H2B | 109.5 | C5—C10—H10 | 119.7 |
| C1—C2—H2B | 109.5 | O4—S2—O6 | 112.61 (13) |
| H2A—C2—H2B | 108.1 | O4—S2—O5 | 111.89 (13) |
| N1—C3—C4 | 109.6 (3) | O6—S2—O5 | 111.41 (13) |

| | | | |
|---|---|---|---|
| N1—C3—H3A | 109.7 | O4—S2—C11 | 106.81 (14) |
| C4—C3—H3A | 109.7 | O6—S2—C11 | 107.45 (14) |
| N1—C3—H3B | 109.7 | O5—S2—C11 | 106.25 (14) |
| C4—C3—H3B | 109.7 | C14—N3—H3NA | 112 (2) |
| H3A—C3—H3B | 108.2 | C14—N3—H3NB | 115 (2) |
| C3—C4—H4A | 109.5 | H3NA—N3—H3NB | 109 (3) |
| C3—C4—H4B | 109.5 | C16—C11—C12 | 119.6 (3) |
| H4A—C4—H4B | 109.5 | C16—C11—S2 | 119.9 (2) |
| C3—C4—H4C | 109.5 | C12—C11—S2 | 120.5 (2) |
| H4A—C4—H4C | 109.5 | C13—C12—C11 | 120.2 (3) |
| H4B—C4—H4C | 109.5 | C13—C12—H12 | 119.9 |
| O2—S1—O1 | 112.42 (14) | C11—C12—H12 | 119.9 |
| O2—S1—O3 | 112.94 (15) | C12—C13—C14 | 120.2 (3) |
| O1—S1—O3 | 112.55 (13) | C12—C13—H13 | 119.9 |
| O2—S1—C5 | 105.94 (14) | C14—C13—H13 | 119.9 |
| O1—S1—C5 | 106.42 (13) | C15—C14—C13 | 119.1 (3) |
| O3—S1—C5 | 105.88 (14) | C15—C14—N3 | 120.4 (3) |
| C8—N2—H2NA | 110.7 (18) | C13—C14—N3 | 120.5 (3) |
| C8—N2—H2NB | 109 (2) | C16—C15—C14 | 120.6 (3) |
| H2NA—N2—H2NB | 105 (3) | C16—C15—H15 | 119.7 |
| C8—N2—H2NC | 110 (2) | C14—C15—H15 | 119.7 |
| H2NA—N2—H2NC | 113 (3) | C15—C16—C11 | 120.2 (3) |
| H2NB—N2—H2NC | 109 (3) | C15—C16—H16 | 119.9 |
| C10—C5—C6 | 120.3 (3) | C11—C16—H16 | 119.9 |
| C10—C5—S1 | 118.9 (2) | | |

| | | | |
|---|---|---|---|
| C3—N1—C2—C1 | 177.1 (3) | S1—C5—C10—C9 | 178.9 (2) |
| C2—N1—C3—C4 | −178.4 (3) | O4—S2—C11—C16 | 47.7 (3) |
| O2—S1—C5—C10 | −165.1 (2) | O6—S2—C11—C16 | −73.4 (3) |
| O1—S1—C5—C10 | 75.1 (3) | O5—S2—C11—C16 | 167.2 (2) |
| O3—S1—C5—C10 | −44.9 (3) | O4—S2—C11—C12 | −132.1 (3) |
| O2—S1—C5—C6 | 16.1 (3) | O6—S2—C11—C12 | 106.9 (3) |
| O1—S1—C5—C6 | −103.7 (3) | O5—S2—C11—C12 | −12.5 (3) |
| O3—S1—C5—C6 | 136.3 (2) | C16—C11—C12—C13 | 1.0 (4) |
| C10—C5—C6—C7 | 2.2 (4) | S2—C11—C12—C13 | −179.3 (2) |
| S1—C5—C6—C7 | −179.0 (2) | C11—C12—C13—C14 | 0.8 (4) |
| C5—C6—C7—C8 | −0.4 (4) | C12—C13—C14—C15 | −2.3 (4) |
| C6—C7—C8—C9 | −1.4 (5) | C12—C13—C14—N3 | −178.8 (3) |
| C6—C7—C8—N2 | 178.0 (3) | C13—C14—C15—C16 | 2.0 (4) |
| C7—C8—C9—C10 | 1.4 (4) | N3—C14—C15—C16 | 178.5 (3) |
| N2—C8—C9—C10 | −178.0 (3) | C14—C15—C16—C11 | −0.2 (5) |
| C8—C9—C10—C5 | 0.5 (4) | C12—C11—C16—C15 | −1.3 (4) |
| C6—C5—C10—C9 | −2.3 (4) | S2—C11—C16—C15 | 179.0 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*NA*···O2 | 0.96 (3) | 1.79 (4) | 2.748 (4) | 175 (3) |

| | | | | |
|---|---|---|---|---|
| N1—H1*NB*···O5 | 0.90 (3) | 2.45 (3) | 3.019 (4) | 122 (3) |
| N1—H1*NB*···O6 | 0.90 (3) | 2.03 (4) | 2.920 (4) | 173 (3) |
| N2—H2*NA*···O4$^{i}$ | 0.94 (2) | 1.88 (2) | 2.794 (4) | 165 (3) |
| N2—H2*NB*···O5$^{ii}$ | 0.94 (2) | 1.85 (2) | 2.778 (3) | 171 (3) |
| N2—H2*NC*···N3$^{iii}$ | 0.97 (2) | 1.85 (2) | 2.812 (4) | 178 (4) |
| N3—H3*NA*···O1$^{iv}$ | 0.83 (4) | 2.21 (4) | 2.998 (4) | 157 (3) |
| N3—H3*NB*···O3$^{v}$ | 0.79 (3) | 2.23 (3) | 2.997 (4) | 164 (3) |
| C3—H3*A*···O3$^{vi}$ | 0.99 | 2.48 | 3.338 (4) | 145 |
| C6—H6···O3$^{vi}$ | 0.95 | 2.65 | 3.507 (4) | 151 |
| C9—H9···O1$^{vii}$ | 0.95 | 2.59 | 3.517 (4) | 165 |

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