# organic compounds

# Sulfonated 1,3-bis(4-pyridyl)propane

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In the title compound, 4-[3-(3-sulfonatopyridin-1-ium-4-yl)-propyl]pyridin-1-ium-3-sulfonate, $C_{13}H_{14}N_2O_6S_2$, the molecule is zwitterionic, with the sulfonic acid proton transfered to the basic pyridine N atom. Also, the structure adopts a butterfly-like conformation with the sulfonate groups on opposite sides of the 'wings'. The dihedral angle between the two pyridinium rings is 83.56 (7)°, and this results in the molecule having a chiral conformation and packing. There is strong intermolecular hydrogen bonding between the pyridinium H and sulfonate O atoms of adjoining molecules. In addition, there are weaker intermolecular C—H···O interactions.

## Related literature

For zwiterionic polymers, see: Estrin & Entelis (1974); Sundaram *et al.* (2010). For 1,3-bis(4-pyridyl)propane ligands, see: Chen *et al.* (2010); Correa *et al.* (2010); Sun *et al.* (2010); Zheng *et al.* (2010). For sulfonation of pyridine rings, see: McElvain & Goese (1943).
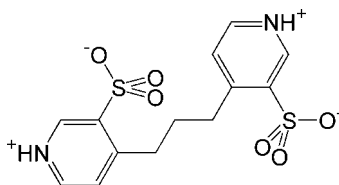


## Experimental

### Crystal data

C₁₃H₁₄N₂O₆S₂  
$M_r = 358.38$  
Orthorhombic, $P2_12_12_1$  
$a = 9.7132$ (2) Å  
$b = 11.2624$ (2) Å  
$c = 13.5369$ (2) Å  

$V = 1480.85$ (5) Å³  
$Z = 4$  
Cu $K\alpha$ radiation  
$\mu = 3.59$ mm⁻¹  
$T = 295$ K  
$0.77 \times 0.25 \times 0.19$ mm  

### Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer  
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2007), based on expressions derived by Clark &

Reid (1995)]  
$T_{min} = 0.290$, $T_{max} = 0.626$  
3960 measured reflections  
2714 independent reflections  
2593 reflections with $I > 2\sigma(I)$  
$R_{int} = 0.021$  

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$  
$wR(F^2) = 0.106$  
$S = 1.06$  
2714 reflections  
208 parameters  
12 restraints  

H-atom parameters constrained  
$\Delta\rho_{max} = 0.51$ e Å⁻³  
$\Delta\rho_{min} = -0.52$ e Å⁻³  
Absolute structure: Flack (1983), 899 Friedel pairs  
Flack parameter: 0.07 (2)  

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1$A$—H1$AA$···O3$A^i$ | 0.86 | 1.88 | 2.706 (3) | 159 |
| N1$A$—H1$AA$···S1$^i$ | 0.86 | 2.79 | 3.633 (3) | 165 |
| N1$B$—H1$BA$···O2$B^{ii}$ | 0.86 | 1.85 | 2.710 (3) | 176 |
| N1$B$—H1$BA$···S2$^{ii}$ | 0.86 | 2.85 | 3.655 (2) | 158 |
| C3$B$—H3$BA$···O1$A^{iii}$ | 0.93 | 2.44 | 3.008 (3) | 119 |
| C4$B$—H4$BA$···O2$A^{iv}$ | 0.93 | 2.50 | 3.035 (3) | 117 |
| C5$B$—H5$BA$···O1$B^v$ | 0.93 | 2.58 | 3.416 (4) | 150 |

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

## References

Chen, Y., Zhou, B., Zhao, J., Li, Y., Su, Z. & Zhao, Z. (2010). *Inorg. Chim. Acta*, **363**, 3897–3903.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Correa, C. C., Diniz, R., Janczak, J., Yoshida, M. I., de Oliveira, L. F. C. & Machado, F. C. (2010). *Polyhedron*, **29**, 3125–3131.
Estrin, Ya. I. & Entelis, S. G. (1974). *Vysokomol. Soedin. Ser. A*, **16**, 1612–19.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
McElvain, S. M. & Goese, M. A. (1943). *J. Am. Chem. Soc.* **65**, 2233–2236.
Oxford Diffraction (2007). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, J.-K., Yao, Q.-X., Ju, Z.-F. & Zhang, J. (2010). *CrystEngComm*, **12**, 1709–1711.
Sundaram, H. S., Cho, Y., Weinman, C. J., Paik, M. Y., Dimitriou, M. D., Finlay, J., Callow, M. E., Callow, J. A., Kramer, E. J. & Ober, C. K. (2010). *Polym. Prepr.* **51**, 384–385.
Zheng, Y.-Q., Zhang, J. & Liu, J.-Y. (2010). *CrystEngComm*, **12**, 2740–2748.

# supporting information

## Sulfonated 1,3-bis(4-pyridyl)propane

**Ore Kuyinu, Andrew P. Purdy and Ray J. Butcher**

### S1. Comment

From the titled compound $C_{13}H_{14}N_2O_6S_2$ we can see that the sulfonatation of 1,3-bis(4-pyridyl)propane occurs in the *meta* position under mercury catalysis, the same as when pyridine is sulfonated under similar conditions (McElvain & Goese, 1943). From recent studies, 1,3-bis(4-pyridyl)propane ligands have been shown (Chen *et al.*, 2010; Correa *et al.*, 2010; Sun *et al.*, 2010; Zheng *et al.*, 2010) to be very flexible, and this has been taken advantage of in supramolecular chemistry. Our interest was to link the sulfonated pyridines into a zwitterionic polymer. (Estrin & Entelis, 1974; Sundaram *et al.*, 2010). Polymer zwitterions are very advantageous in the sense that their distinct polar ends have high electric dipoles, and can readily reorient to an applied electric field if the chain is flexible.

In view of the interest in a flexible zwitterionic polymer backbone, the starting material, 1,3-bis(4-pyridyl)propane was sulfonated. The structure of this derivative is reported here. The structure shows that both pyridine rings have been sulfonated in the 3-position. As is to be expected for a moiety containing both acidic and basic substituents, the molecule is zwitterionic, with the sulfonic acid proton transfered to the basic pyridine N. The structure has adopted a "butterfly-like" conformation with the sulfonate groups on opposite sides of the "wings". The dihedral angle of 83.56 (7)° between the two pyridinium rings is shown in Figure 2. This has resulted in the molecule being chiral in the solid state even though it is not chiral in solution. There is strong intermolecular hydrogen bonding between the pyridinium H and sulfonate O atoms of adjoining molecules. In addition there are weaker intermolecular C—H···O interactions.

### S2. Experimental

The compound was prepared by adding a mercury catalyst (0.05 g) to 0.33 g of 1,3-bis(4-pyridyl)propane dissolved in 3.24 g of fuming sulfuric acid (oleum). The reaction mixture was placed in a quartz tube that was sealed under vacuum with a fill factor of 10/15.4 cm. The quartz tube was then placed into a pressurized hydrothermal vessel that was set in a furnace at a temperature of 245°C. The pressure vessel attained an internal temperature of 204°C, and the reaction continued for 5 days. After cooling, the quartz tube was removed from the chamber behind a blast shield in a fume hood, and was frozen with liquid nitrogen before opening. The liquid was then poured into an Erlenmeyer flask containing about 10 ml of triply distilled water and was allowed to stand. Crystals of the titled compound slowly appeared over a month at which point they were washed with alcohol and allowed to air dry on top of the oven at about 50°C. Approximately 0.15 g was isolated (25%). MP: dec 320. NMR: (D$_2$O/DSS): $^1$H, 2.28 (CH$_2$, 2H), 3.44 (CH$_2$, 4H), 8.13 (py, 2H), 8.79 (py, 2H), 9.13 (py, 2H); $^{13}$C 31.75 (CH$_2$, 1 C), 35.39 (CH$_2$, 2 C), 131.97, 142.50, 144.09, 145.02, 164.74 (py).

### S3. Refinement

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with a C—H distance of 0.93 and 0.97 Å $U_{iso}$(H) = 1.2$U_{eq}$(C). The H atoms attached to N were idealized with an N–H distance of 0.86

Å.
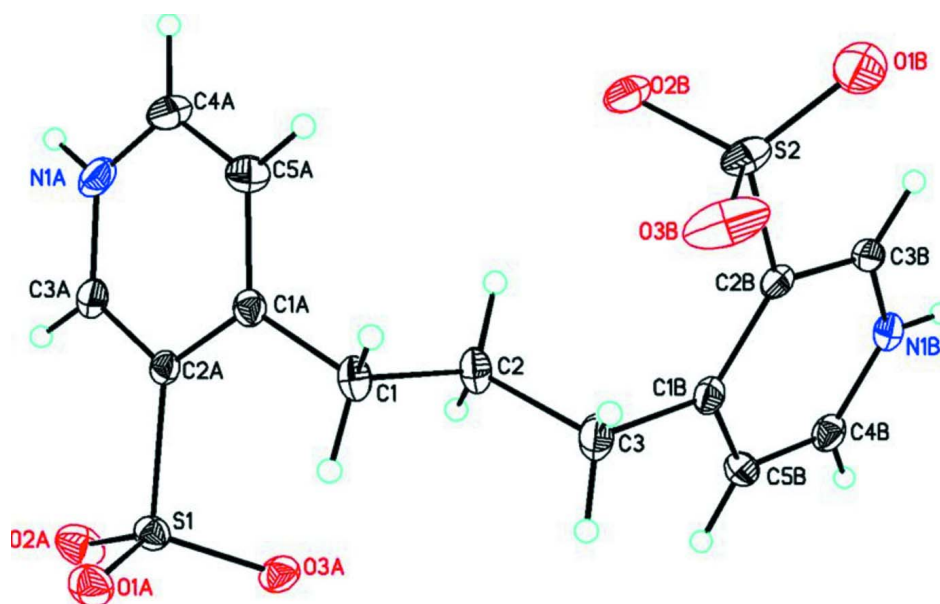


**Figure 1**

Diagram of $C_{13}H_{14}N_2O_6S_2$ illustrating the atom numbering scheme used. Thermal ellipsoids are at the 30% probability level.
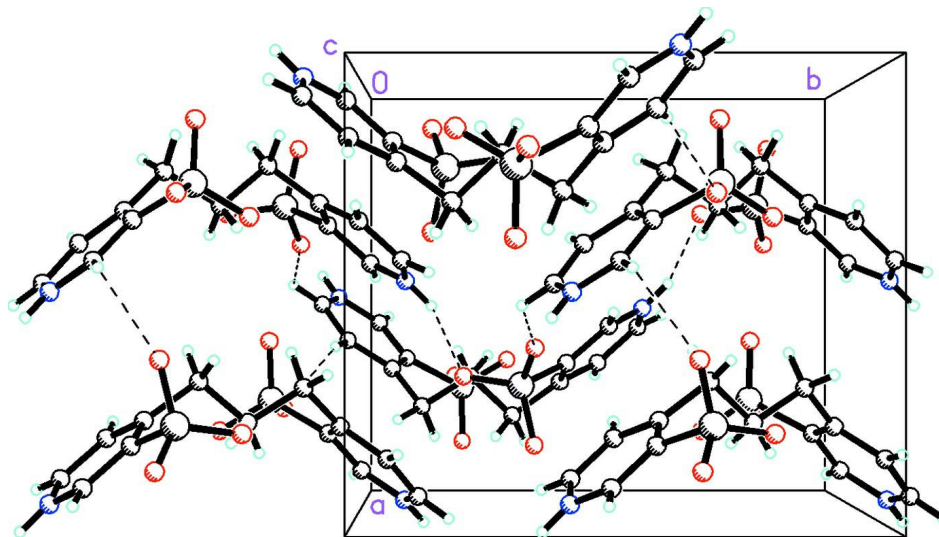


**Figure 2**

The molecular packing for $C_{13}H_{14}N_2O_6S_2$ viewed down the *c* axis showing the hydrogen bonds as dashed lines.

**4-[3-(3-sulfonatopyridin-1-ium-4-yl)propyl]pyridin-1-ium-3-sulfonate**

*Crystal data*

| | |
|---|---|
| $C_{13}H_{14}N_2O_6S_2$ | $c = 13.5369$ (2) Å |
| $M_r = 358.38$ | $V = 1480.85$ (5) Å³ |
| Orthorhombic, $P2_12_12_1$ | $Z = 4$ |
| $a = 9.7132$ (2) Å | $F(000) = 744$ |
| $b = 11.2624$ (2) Å | $D_x = 1.607$ Mg m⁻³ |

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 3437 reflections

$\theta = 4.6–77.4°$

$\mu = 3.59$ mm$^{-1}$

$T = 295$ K

Needle, pale yellow

$0.77 \times 0.25 \times 0.19$ mm

*Data collection*

Oxford Diffraction Xcalibur Ruby Gemini diffractometer

Radiation source: Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.5081 pixels mm$^{-1}$

$\omega$ scans

Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2007), based on expressions derived by Clark & Reid (1995)]

$T_{min} = 0.290$, $T_{max} = 0.626$

3960 measured reflections

2714 independent reflections

2593 reflections with $I > 2\sigma(I)$

$R_{int} = 0.021$

$\theta_{max} = 77.6°$, $\theta_{min} = 5.1°$

$h = -8 \rightarrow 12$

$k = -11 \rightarrow 14$

$l = -16 \rightarrow 13$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

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

$wR(F^2) = 0.106$

$S = 1.06$

2714 reflections

208 parameters

12 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

$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.3816P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.51$ e Å$^{-3}$

$\Delta\rho_{min} = -0.52$ e Å$^{-3}$

Absolute structure: Flack (1983), 899 Friedel pairs

Absolute structure parameter: 0.07 (2)

*Special details*

**Experimental**. CrysAlis Pro (Oxford Diffraction, 2007) Analytical numeric absorption correction using a multifaceted crystal model, based on expressions derived by Clark & Reid (1995)

**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$^2$)*

|  | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.28273 (7) | 0.82506 (6) | 0.18353 (4) | 0.03490 (17) |
| S2 | 0.25484 (7) | 0.69702 (6) | 0.73312 (6) | 0.0450 (2) |
| O1A | 0.1398 (2) | 0.8521 (2) | 0.16464 (17) | 0.0501 (6) |
| O2A | 0.3744 (3) | 0.8523 (3) | 0.10328 (15) | 0.0587 (7) |
| O3A | 0.3027 (2) | 0.70553 (17) | 0.22295 (16) | 0.0444 (5) |
| O1B | 0.2815 (3) | 0.6781 (2) | 0.8361 (2) | 0.0741 (8) |
| O2B | 0.3281 (3) | 0.80026 (19) | 0.69595 (18) | 0.0521 (5) |

| | | | | |
|---|---|---|---|---|
| O3B | 0.1119 (3) | 0.6967 (3) | 0.7050 (3) | 0.0883 (11) |
| N1A | 0.4665 (3) | 1.0862 (2) | 0.3287 (2) | 0.0478 (6) |
| H1AA | 0.5265 | 1.1394 | 0.3135 | 0.057* |
| N1B | 0.4929 (2) | 0.4168 (2) | 0.68491 (18) | 0.0356 (5) |
| H1BA | 0.5502 | 0.3772 | 0.7204 | 0.043* |
| C1 | 0.1965 (3) | 0.8097 (3) | 0.41421 (19) | 0.0386 (6) |
| H1A | 0.1477 | 0.7738 | 0.3593 | 0.046* |
| H1B | 0.1293 | 0.8374 | 0.4620 | 0.046* |
| C2 | 0.2932 (3) | 0.7187 (3) | 0.4620 (2) | 0.0424 (6) |
| H2A | 0.3445 | 0.7570 | 0.5147 | 0.051* |
| H2B | 0.3588 | 0.6912 | 0.4131 | 0.051* |
| C3 | 0.2151 (3) | 0.6114 (3) | 0.5045 (2) | 0.0479 (7) |
| H3A | 0.1350 | 0.6384 | 0.5409 | 0.057* |
| H3B | 0.1841 | 0.5605 | 0.4512 | 0.057* |
| C1A | 0.2832 (3) | 0.9119 (2) | 0.37844 (17) | 0.0326 (5) |
| C2A | 0.3323 (3) | 0.9228 (2) | 0.28185 (18) | 0.0301 (5) |
| C3A | 0.4240 (3) | 1.0107 (2) | 0.2592 (2) | 0.0391 (6) |
| H3AA | 0.4569 | 1.0178 | 0.1950 | 0.047* |
| C4A | 0.4185 (4) | 1.0818 (3) | 0.4211 (3) | 0.0553 (9) |
| H4AA | 0.4473 | 1.1374 | 0.4675 | 0.066* |
| C5A | 0.3276 (4) | 0.9959 (3) | 0.4470 (2) | 0.0486 (7) |
| H5AA | 0.2945 | 0.9929 | 0.5114 | 0.058* |
| C1B | 0.3094 (3) | 0.5428 (2) | 0.57229 (19) | 0.0356 (5) |
| C2B | 0.3329 (3) | 0.5730 (2) | 0.67150 (19) | 0.0310 (5) |
| C3B | 0.4251 (3) | 0.5075 (2) | 0.72588 (19) | 0.0338 (5) |
| H3BA | 0.4405 | 0.5264 | 0.7918 | 0.041* |
| C4B | 0.4747 (3) | 0.3857 (2) | 0.5911 (2) | 0.0401 (6) |
| H4BA | 0.5246 | 0.3229 | 0.5645 | 0.048* |
| C5B | 0.3826 (3) | 0.4462 (3) | 0.53385 (19) | 0.0414 (6) |
| H5BA | 0.3684 | 0.4230 | 0.4687 | 0.050* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.0363 (3) | 0.0368 (3) | 0.0316 (3) | 0.0032 (3) | −0.0007 (2) | −0.0034 (2) |
| S2 | 0.0395 (4) | 0.0328 (3) | 0.0627 (4) | −0.0030 (3) | 0.0108 (3) | −0.0146 (3) |
| O1A | 0.0454 (12) | 0.0517 (13) | 0.0531 (12) | 0.0097 (10) | −0.0129 (9) | −0.0057 (10) |
| O2A | 0.0598 (14) | 0.0826 (18) | 0.0336 (9) | −0.0084 (14) | 0.0095 (10) | −0.0077 (11) |
| O3A | 0.0485 (11) | 0.0315 (9) | 0.0532 (11) | 0.0056 (9) | −0.0039 (9) | −0.0078 (8) |
| O1B | 0.102 (2) | 0.0568 (14) | 0.0640 (14) | 0.0053 (16) | 0.0363 (15) | −0.0128 (12) |
| O2B | 0.0640 (14) | 0.0320 (10) | 0.0604 (13) | −0.0069 (10) | −0.0061 (11) | −0.0096 (9) |
| O3B | 0.0386 (12) | 0.0712 (18) | 0.155 (3) | 0.0011 (13) | 0.0049 (16) | −0.055 (2) |
| N1A | 0.0484 (14) | 0.0281 (11) | 0.0669 (17) | −0.0097 (10) | −0.0099 (13) | 0.0047 (11) |
| N1B | 0.0359 (11) | 0.0312 (10) | 0.0396 (11) | 0.0001 (9) | 0.0002 (9) | 0.0083 (9) |
| C1 | 0.0378 (13) | 0.0425 (14) | 0.0354 (11) | 0.0022 (12) | 0.0038 (10) | 0.0110 (11) |
| C2 | 0.0405 (14) | 0.0468 (14) | 0.0401 (13) | −0.0009 (13) | 0.0002 (12) | 0.0174 (11) |
| C3 | 0.0466 (16) | 0.0459 (15) | 0.0511 (15) | −0.0080 (14) | −0.0070 (14) | 0.0181 (13) |
| C1A | 0.0353 (12) | 0.0307 (11) | 0.0319 (11) | 0.0061 (11) | 0.0011 (10) | 0.0021 (9) |

| | | | | | |
|---|---|---|---|---|---|
| C2A | 0.0327 (11) | 0.0260 (10) | 0.0314 (10) | 0.0043 (10) | −0.0011 (9) | 0.0024 (9) |
| C3A | 0.0415 (14) | 0.0333 (12) | 0.0425 (14) | −0.0003 (11) | −0.0002 (11) | 0.0086 (11) |
| C4A | 0.071 (2) | 0.0360 (15) | 0.0585 (18) | −0.0021 (15) | −0.0121 (17) | −0.0129 (14) |
| C5A | 0.0600 (19) | 0.0457 (16) | 0.0401 (14) | 0.0031 (15) | 0.0010 (13) | −0.0098 (12) |
| C1B | 0.0388 (13) | 0.0312 (12) | 0.0368 (12) | −0.0063 (11) | 0.0020 (11) | 0.0079 (10) |
| C2B | 0.0337 (12) | 0.0230 (10) | 0.0363 (12) | −0.0032 (9) | 0.0067 (10) | −0.0013 (9) |
| C3B | 0.0383 (12) | 0.0332 (12) | 0.0299 (11) | −0.0069 (10) | 0.0025 (10) | −0.0008 (10) |
| C4B | 0.0488 (15) | 0.0286 (12) | 0.0428 (14) | 0.0014 (12) | 0.0105 (12) | −0.0010 (11) |
| C5B | 0.0557 (16) | 0.0412 (14) | 0.0272 (11) | −0.0061 (14) | 0.0046 (11) | −0.0023 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O2A | 1.438 (2) | C2—H2A | 0.9700 |
| S1—O1A | 1.444 (2) | C2—H2B | 0.9700 |
| S1—O3A | 1.461 (2) | C3—C1B | 1.509 (4) |
| S1—C2A | 1.793 (3) | C3—H3A | 0.9700 |
| S2—O1B | 1.433 (3) | C3—H3B | 0.9700 |
| S2—O3B | 1.439 (3) | C1A—C5A | 1.394 (4) |
| S2—O2B | 1.453 (2) | C1A—C2A | 1.397 (3) |
| S2—C2B | 1.795 (2) | C2A—C3A | 1.366 (4) |
| N1A—C3A | 1.334 (4) | C3A—H3AA | 0.9300 |
| N1A—C4A | 1.337 (5) | C4A—C5A | 1.356 (5) |
| N1A—H1AA | 0.8600 | C4A—H4AA | 0.9300 |
| N1B—C4B | 1.329 (4) | C5A—H5AA | 0.9300 |
| N1B—C3B | 1.336 (3) | C1B—C5B | 1.400 (4) |
| N1B—H1BA | 0.8600 | C1B—C2B | 1.404 (4) |
| C1—C1A | 1.506 (4) | C2B—C3B | 1.375 (4) |
| C1—C2 | 1.534 (4) | C3B—H3BA | 0.9300 |
| C1—H1A | 0.9700 | C4B—C5B | 1.366 (4) |
| C1—H1B | 0.9700 | C4B—H4BA | 0.9300 |
| C2—C3 | 1.539 (4) | C5B—H5BA | 0.9300 |
| | | | |
| O2A—S1—O1A | 114.62 (15) | C1B—C3—H3B | 109.8 |
| O2A—S1—O3A | 112.98 (15) | C2—C3—H3B | 109.8 |
| O1A—S1—O3A | 112.74 (14) | H3A—C3—H3B | 108.3 |
| O2A—S1—C2A | 105.27 (13) | C5A—C1A—C2A | 117.2 (3) |
| O1A—S1—C2A | 105.09 (12) | C5A—C1A—C1 | 118.5 (2) |
| O3A—S1—C2A | 105.00 (11) | C2A—C1A—C1 | 124.0 (2) |
| O1B—S2—O3B | 115.5 (2) | C3A—C2A—C1A | 119.8 (2) |
| O1B—S2—O2B | 111.54 (16) | C3A—C2A—S1 | 116.9 (2) |
| O3B—S2—O2B | 112.5 (2) | C1A—C2A—S1 | 123.30 (19) |
| O1B—S2—C2B | 105.08 (15) | N1A—C3A—C2A | 120.4 (3) |
| O3B—S2—C2B | 106.43 (15) | N1A—C3A—H3AA | 119.8 |
| O2B—S2—C2B | 104.76 (13) | C2A—C3A—H3AA | 119.8 |
| C3A—N1A—C4A | 121.9 (3) | N1A—C4A—C5A | 119.7 (3) |
| C3A—N1A—H1AA | 119.1 | N1A—C4A—H4AA | 120.1 |
| C4A—N1A—H1AA | 119.1 | C5A—C4A—H4AA | 120.1 |
| C4B—N1B—C3B | 122.2 (2) | C4A—C5A—C1A | 120.9 (3) |

| | | | |
|---|---|---|---|
| C4B—N1B—H1BA | 118.9 | C4A—C5A—H5AA | 119.5 |
| C3B—N1B—H1BA | 118.9 | C1A—C5A—H5AA | 119.5 |
| C1A—C1—C2 | 107.7 (2) | C5B—C1B—C2B | 117.5 (2) |
| C1A—C1—H1A | 110.2 | C5B—C1B—C3 | 118.7 (3) |
| C2—C1—H1A | 110.2 | C2B—C1B—C3 | 123.8 (3) |
| C1A—C1—H1B | 110.2 | C3B—C2B—C1B | 119.2 (2) |
| C2—C1—H1B | 110.2 | C3B—C2B—S2 | 116.38 (19) |
| H1A—C1—H1B | 108.5 | C1B—C2B—S2 | 124.4 (2) |
| C1—C2—C3 | 112.4 (2) | N1B—C3B—C2B | 120.6 (2) |
| C1—C2—H2A | 109.1 | N1B—C3B—H3BA | 119.7 |
| C3—C2—H2A | 109.1 | C2B—C3B—H3BA | 119.7 |
| C1—C2—H2B | 109.1 | N1B—C4B—C5B | 119.9 (3) |
| C3—C2—H2B | 109.1 | N1B—C4B—H4BA | 120.1 |
| H2A—C2—H2B | 107.9 | C5B—C4B—H4BA | 120.1 |
| C1B—C3—C2 | 109.3 (2) | C4B—C5B—C1B | 120.6 (2) |
| C1B—C3—H3A | 109.8 | C4B—C5B—H5BA | 119.7 |
| C2—C3—H3A | 109.8 | C1B—C5B—H5BA | 119.7 |
| | | | |
| C1A—C1—C2—C3 | 178.2 (2) | C1—C1A—C5A—C4A | 172.4 (3) |
| C1—C2—C3—C1B | −165.5 (3) | C2—C3—C1B—C5B | −94.3 (3) |
| C2—C1—C1A—C5A | −78.8 (3) | C2—C3—C1B—C2B | 82.9 (3) |
| C2—C1—C1A—C2A | 95.4 (3) | C5B—C1B—C2B—C3B | −0.1 (4) |
| C5A—C1A—C2A—C3A | 2.3 (4) | C3—C1B—C2B—C3B | −177.4 (3) |
| C1—C1A—C2A—C3A | −172.0 (2) | C5B—C1B—C2B—S2 | 177.4 (2) |
| C5A—C1A—C2A—S1 | −178.4 (2) | C3—C1B—C2B—S2 | 0.2 (4) |
| C1—C1A—C2A—S1 | 7.3 (4) | O1B—S2—C2B—C3B | −15.5 (3) |
| O2A—S1—C2A—C3A | 9.9 (2) | O3B—S2—C2B—C3B | −138.4 (3) |
| O1A—S1—C2A—C3A | −111.5 (2) | O2B—S2—C2B—C3B | 102.2 (2) |
| O3A—S1—C2A—C3A | 129.4 (2) | O1B—S2—C2B—C1B | 166.9 (2) |
| O2A—S1—C2A—C1A | −169.4 (2) | O3B—S2—C2B—C1B | 44.0 (3) |
| O1A—S1—C2A—C1A | 69.2 (2) | O2B—S2—C2B—C1B | −75.4 (2) |
| O3A—S1—C2A—C1A | −50.0 (2) | C4B—N1B—C3B—C2B | −0.1 (4) |
| C4A—N1A—C3A—C2A | −2.3 (5) | C1B—C2B—C3B—N1B | 0.7 (4) |
| C1A—C2A—C3A—N1A | −0.2 (4) | S2—C2B—C3B—N1B | −177.00 (19) |
| S1—C2A—C3A—N1A | −179.5 (2) | C3B—N1B—C4B—C5B | −1.0 (4) |
| C3A—N1A—C4A—C5A | 2.4 (5) | N1B—C4B—C5B—C1B | 1.6 (4) |
| N1A—C4A—C5A—C1A | −0.1 (5) | C2B—C1B—C5B—C4B | −1.0 (4) |
| C2A—C1A—C5A—C4A | −2.2 (5) | C3—C1B—C5B—C4B | 176.4 (3) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1*A*—H1*AA*···O3*A*[i] | 0.86 | 1.88 | 2.706 (3) | 159 |
| N1*A*—H1*AA*···S1[i] | 0.86 | 2.79 | 3.633 (3) | 165 |
| N1*B*—H1*BA*···O2*B*[ii] | 0.86 | 1.85 | 2.710 (3) | 176 |
| N1*B*—H1*BA*···S2[ii] | 0.86 | 2.85 | 3.655 (2) | 158 |
| C3*B*—H3*BA*···O1*A*[iii] | 0.93 | 2.44 | 3.008 (3) | 119 |

| | | | |
|---|---|---|---|
| C4*B*—H4*BA*···O2*A*[iv] | 0.93 | 2.50 | 3.035 (3) | 117 |
| C5*B*—H5*BA*···O1*B*[v] | 0.93 | 2.58 | 3.416 (4) | 150 |

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) *x*+1/2, −*y*+3/2, −*z*+1; (iv) −*x*+1, *y*−1/2, −*z*+1/2; (v) −*x*+1/2, −*y*+1, *z*−1/2.