



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

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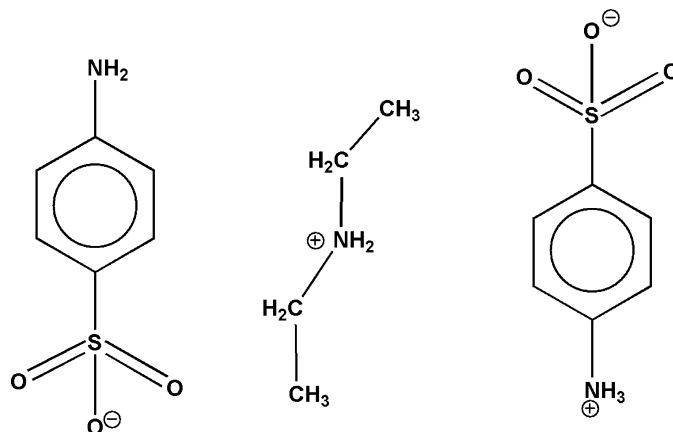
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The title compound, $C_4H_{12}N^+ \cdot C_6H_6NO_3S^- \cdot C_6H_7NO_3S$, consists of an ion pair and a zwitterionic neutral molecule. The cation adopts an extended conformation [C—C—N—C torsion angles = 177.1 (3) and -178.4 (3)°]. In the crystal, 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

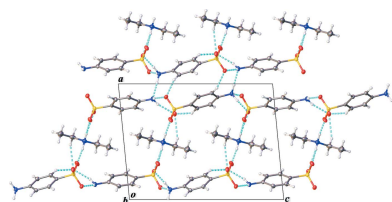
Acids such as sulfuric, nitric, oxalic, phosphoric, substituted sulfonic, etc. when mixed in water with amines give acidic or neutral salts that may be soluble in organic solvents: this solubility allows for the study of their interactions with metal halides, acetates, nitrates, perchlorates, etc, which 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



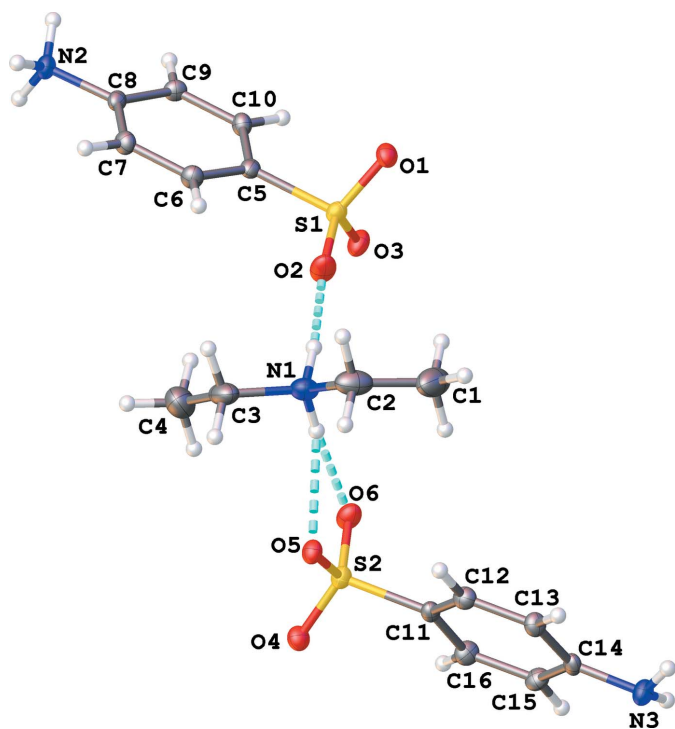


Figure 1
The molecular structure of the title compound. Displacement ellipsoids depicted at the 50% probability level and H atoms as spheres of an arbitrary radius. Hydrogen bonds are represented by light-blue dashed lines.

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, °).

<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–H1NA···O2	0.96 (3)	1.79 (4)	2.748 (4)	175 (3)
N1–H1NB···O5	0.90 (3)	2.45 (3)	3.019 (4)	122 (3)
N1–H1NB···O6	0.90 (3)	2.03 (4)	2.920 (4)	173 (3)
N2–H2NA···O4 ⁱ	0.94 (2)	1.88 (2)	2.794 (4)	165 (3)
N2–H2NB···O5 ⁱⁱ	0.94 (2)	1.85 (2)	2.778 (3)	171 (3)
N2–H2NC···N3 ⁱⁱⁱ	0.97 (2)	1.85 (2)	2.812 (4)	178 (4)
N3–H3NA···O1 ^{iv}	0.83 (4)	2.21 (4)	2.998 (4)	157 (3)
N3–H3NB···O3 ^v	0.79 (3)	2.23 (3)	2.997 (4)	164 (3)
C3–H3A···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–H2NA···O4ⁱ, N2–H2NB···O5ⁱⁱ, N2–H2NC···N3ⁱⁱⁱ, N3–H3NA···O1^{iv} and N3–H3NB···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–H1NA···O2, N1–H1NB···O5 and N1–H1NB···O6 hydrogen bonds, yielding a three-dimensional network (Fig. 2). Some weak C–H···O (C3–H3A···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

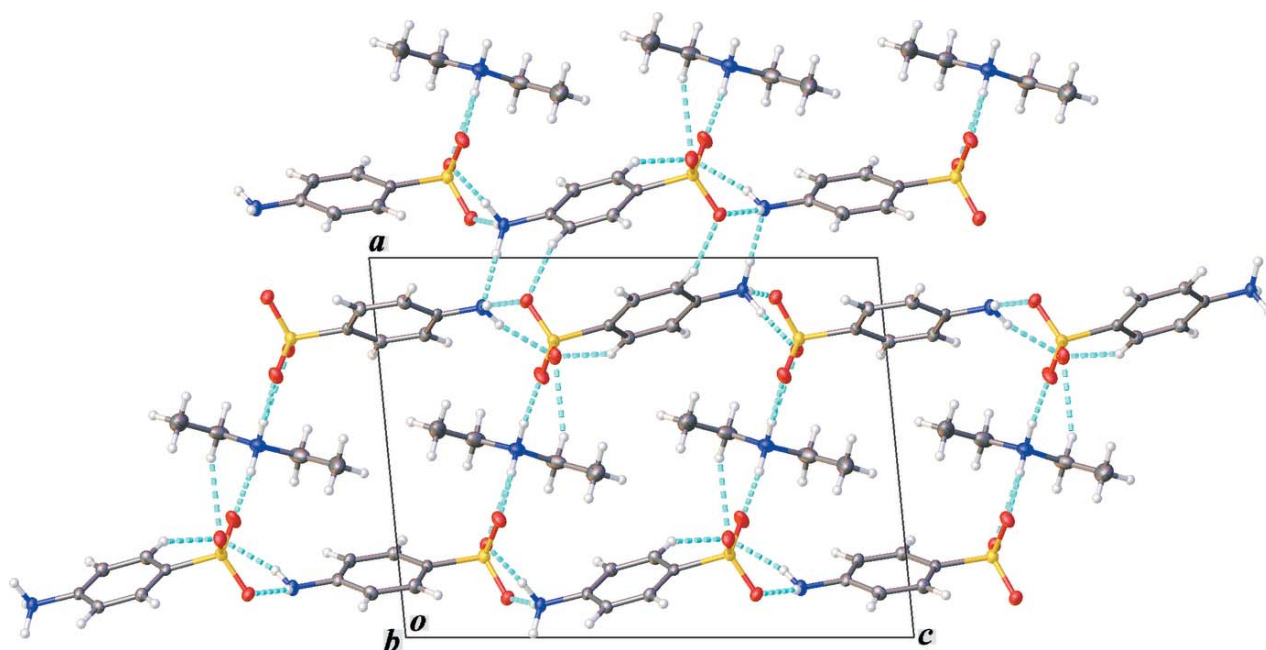


Figure 2
Packing diagram, viewed along the *b* axis. Hydrogen bonds are represented by light-blue dashed lines.

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).

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	C ₄ H ₁₂ N ⁺ ·C ₆ H ₆ NO ₃ S ⁻ ·C ₆ H ₇ NO ₃ S
<i>M_r</i>	419.51
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.419 (3), 5.6731 (16), 15.226 (4)
β (°)	95.530 (4)
<i>V</i> (Å ³)	981.8 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.31
Crystal size (mm)	0.22 × 0.19 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.781, 0.931
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	18906, 4911, 4228
<i>R</i> _{int}	0.056
(sin θ/λ) _{max} (Å ⁻¹)	0.668
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.29, -0.38
Absolute structure	Flack <i>x</i> determined using 1632 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.03 (6)

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

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supporting information

Acta Cryst. (2016). E72, 1830-1832 [https://doi.org/10.1107/S2056989016018041]

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

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (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

$C_4H_{12}N^+ \cdot C_6H_6NO_3S^- \cdot C_6H_7NO_3S$

$M_r = 419.51$

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) Å³

$Z = 2$

$F(000) = 444$

$D_x = 1.419$ 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

$0.22 \times 0.19 \times 0.05$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm⁻¹

combination of ω and φ -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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.056$

$\theta_{\max} = 28.4$ °, $\theta_{\min} = 1.3$ °

$h = -15$ → 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 (\AA^2)

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

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 (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1NA \cdots O2	0.96 (3)	1.79 (4)	2.748 (4)	175 (3)

N1—H1NB···O5	0.90 (3)	2.45 (3)	3.019 (4)	122 (3)
N1—H1NB···O6	0.90 (3)	2.03 (4)	2.920 (4)	173 (3)
N2—H2NA···O4 ⁱ	0.94 (2)	1.88 (2)	2.794 (4)	165 (3)
N2—H2NB···O5 ⁱⁱ	0.94 (2)	1.85 (2)	2.778 (3)	171 (3)
N2—H2NC···N3 ⁱⁱⁱ	0.97 (2)	1.85 (2)	2.812 (4)	178 (4)
N3—H3NA···O1 ^{iv}	0.83 (4)	2.21 (4)	2.998 (4)	157 (3)
N3—H3NB···O3 ^v	0.79 (3)	2.23 (3)	2.997 (4)	164 (3)
C3—H3A···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) $-x, y+1/2, -z+1$.