

## 2,3-Dimethyl-1*H*-imidazol-3-ium benzene-sulfonate–1,2-dimethyl-1*H*-imidazole co-crystal

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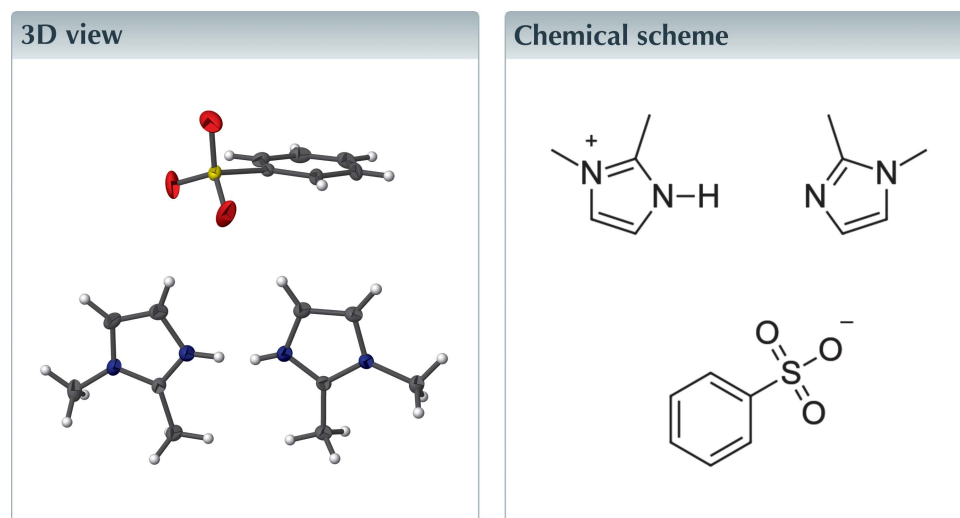
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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

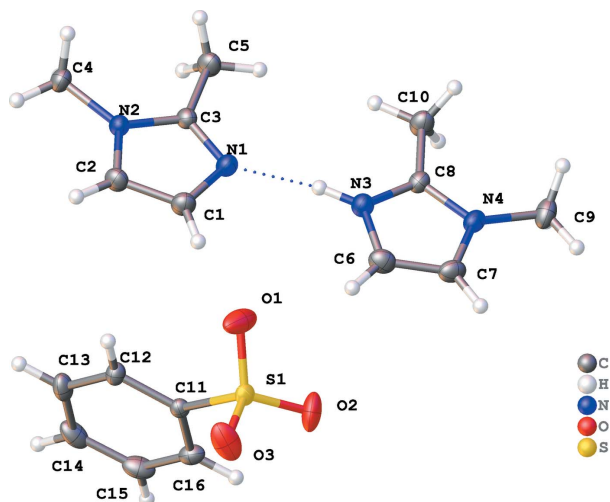
In the title co-crystal,  $C_5H_9N_2^+ \cdot C_6H_5O_3S^- \cdot C_5H_8N_2$ , the two 1,2-dimethylimidazole rings exist as partially protonated moieties in the asymmetric unit as a two-part disordered unit wherein the acidic hydrogen atom is bound to each ring. The two imidazolium cations share a strong hydrogen bond *via* the acidic hydrogen atom, which is disordered between two positions, being bonded to the first *versus* second imidazole ring in a 0.33 (2) to 0.67 (2) ratio. A benzene sulfonate anion is present for charge balance and interacts with the aromatic H atoms on both imidazole rings as well as with the methyl groups on the rings.



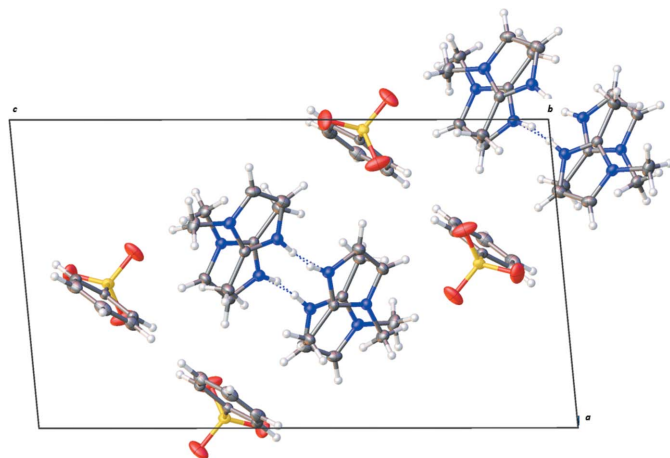
### Structure description

The title compound (Fig. 1) crystallizes with two 1,2-dimethylimidazolium cations in the asymmetric unit. The two imidazole rings are each partially protonated, wherein the acidic hydrogen atom is bound between the two N atoms of the aromatic ring in a 0.33 (2) to 0.67 (2) ratio. Hydrogen bonding appears to be the dominant intermolecular interaction with each molecule or ion exhibiting interactions (Fig. 2). For instance, the shortest hydrogen bonds are N–H...N links between the imidazolium rings with H...N = 1.83 (8) and 1.90 (8) Å. This bonding arises from the disordered hydrogen atom, which appears to be shared between the two rings. Further, cation–anion C–H...O interactions occur between the aromatic H atoms and the sulfonate O atoms. Finally, there are anion–anion interactions wherein O atoms of the sulfonate group interact with hydrogens on the benzene rings. A summary of the distances for the hydrogen bonds is found in Table 1.

For a related structure with a chloride anion, see Kelley *et al.* (2013).



**Figure 1**  
The title compound shown with 50% probability ellipsoids. Only the major component is shown.



**Figure 2**  
Packing diagram of the title compound viewed down the (010) plane showing a layered network of ion pairs held together through hydrogen interactions. Both parts of the disorder are shown.

### Synthesis and crystallization

The reaction was conducted in a Biotage Initiator+ microwave reactor. To a microwave vial was added a stir bar as well as 7.5 mmol (721 mg) of 1,2 dimethylimidazole and 7.5 mmol (901  $\mu$ L) of benzenesulfonyl fluoride. The vial was sealed and placed into the microwave reactor. The reaction was performed at 105°C for 5 minutes and 38 s with very high microwave absorption, stirring at 600 rpm. Once finished and cooled to room temperature, the solution was transferred to an oven-dried amber scintillation vial and sealed with parafilm. After one week, crystals suitable for diffraction were found growing in the vial.

A proposed mechanism leading to the formation of the crystallized product reported herein is shown in Fig. 3.

$^1\text{H}$  NMR (400 MHz, chloroform- $D$ )  $\delta$  8.01–7.99 (*m*, 1H), 7.89–7.87 (*m*, 1H), 7.77 (*dd*,  $J = 8.1, 6.7$  Hz, 1H), 7.62 (*t*,  $J = 7.4$  Hz, 1H), 7.35 (*t*,  $J = 2.6$  Hz, 1H), 7.25 (*s*, 1H), 6.98–6.83 (*m*, 2H), 3.61 (*d*,  $J = 9.1$  Hz, 3H), 2.46 (*d*,  $J = 14.0$  Hz, 3H)

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots N3$	0.83	1.90	2.6970 (11)	163
$N3-H3N\cdots N1$	0.89	1.81	2.6970 (11)	170
$C1-H1\cdots O1$	0.95	2.43	3.3741 (13)	170
$C4-H4B\cdots O3^i$	0.98	2.33	3.2956 (12)	170
$C6-H6\cdots O2$	0.95	2.60	3.4288 (14)	146
$C7-H7\cdots O2^{ii}$	0.95	2.41	3.3254 (12)	162
$C9-H9A\cdots O3^{iii}$	0.98	2.53	3.4846 (14)	164
$C9-H9B\cdots O3^{ii}$	0.98	2.46	3.4381 (14)	173
$C13-H13\cdots O1^i$	0.95	2.67	3.4738 (14)	143
$C14-H14\cdots O1^{iv}$	0.95	2.48	3.3920 (13)	162

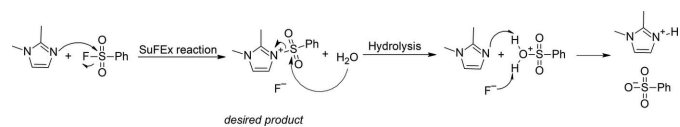
Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iv)  $x, y - 1, z$ .

**Table 2**  
Experimental details.

Crystal data	$C_5H_9N_2^+ \cdot C_6H_5O_3S^- \cdot C_5H_8N_2$
Chemical formula	350.43
$M_r$	Monoclinic, $P2_1/n$
Crystal system, space group	150
Temperature (K)	10.8820 (6), 8.4029 (4), 18.9678 (11)
$a, b, c$ ( $\text{\AA}$ )	$\beta$ ( $^\circ$ ) 95.440 (2)
$V$ ( $\text{\AA}^3$ )	1726.61 (16)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	0.21
Crystal size (mm)	$0.55 \times 0.42 \times 0.33$
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}, T_{\max}$	0.716, 0.747
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	74762, 6612, 5787
$R_{\text{int}}$	0.032
$(\sin \theta/\lambda)_{\text{max}}$ ( $\text{\AA}^{-1}$ )	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.095, 1.05
No. of reflections	6612
No. of parameters	225
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ( $e \text{\AA}^{-3}$ )	0.40, $-0.44$

Computer programs: APEX3 and SAINT (Bruker, 2018), SHELXS97 (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2015), shelXle (Hübschle *et al.*, 2011), OLEX2 (Dolomanov *et al.*, 2009), publCIF (Westrip, 2010) and enCIFer (Allen *et al.*, 2004).

$^{13}\text{C}$  NMR (101 MHz, chloroform- $D$ )  $\delta$  206.7, 144.8, 135.7, 130.0, 129.8, 128.5, 128.3, 126.0, 121.2, 121.0, 77.4, 77.1, 76.8, 76.6, 33.5, 12.0,  $-1.6$ .



**Figure 3**  
Proposed mechanism leading to the formation of the crystallized product reported herein.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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## full crystallographic data

*IUCrData* (2020). 5, x200689 [https://doi.org/10.1107/S2414314620006896]

## 2,3-Dimethyl-1*H*-imidazol-3-ium benzenesulfonate–1,2-dimethyl-1*H*-imidazole co-crystal

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2,3-Dimethyl-1*H*-imidazol-3-ium benzenesulfonate; 1,2-dimethyl-1*H*-imidazole

### Crystal data

$C_5H_9N_2^+ \cdot C_6H_5O_3S^- \cdot C_5H_8N_2$

$M_r = 350.43$

Monoclinic,  $P2_1/n$

$a = 10.8820$  (6) Å

$b = 8.4029$  (4) Å

$c = 18.9678$  (11) Å

$\beta = 95.440$  (2)°

$V = 1726.61$  (16) Å<sup>3</sup>

$Z = 4$

$F(000) = 744$

$D_x = 1.348$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9689 reflections

$\theta = 2.7$ – $33.2$ °

$\mu = 0.21$  mm<sup>-1</sup>

$T = 150$  K

Block, colourless

$0.55 \times 0.42 \times 0.33$  mm

### Data collection

Bruker AXS D8 Quest CMOS  
diffractometer

Radiation source: fine focus sealed tube X-ray  
source

Triumph curved graphite crystal  
monochromator

Detector resolution: 10.4167 pixels mm<sup>-1</sup>

$\omega$  and  $\phi$  scans

Absorption correction: multi-scan  
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.716$ ,  $T_{\max} = 0.747$

74762 measured reflections

6612 independent reflections

5787 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 33.2$ °,  $\theta_{\min} = 2.3$ °

$h = -16 \rightarrow 16$

$k = -12 \rightarrow 12$

$l = -29 \rightarrow 28$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.095$

$S = 1.05$

6612 reflections

225 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 atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.6618P]$

where  $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.40$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.44$  e Å<sup>-3</sup>

Extinction correction: SHELXL-2018/3  
(Sheldrick 2015),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0085 (10)

*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.

**Refinement.** H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms. C—H bond distances were constrained to 0.95 Å for aromatic and alkene C—H moieties, and to 0.98 Å for CH<sub>3</sub> moieties, respectively. The N—H proton hydrogen bonding between atoms N1 and N3 was found to be disordered and was refined as split between two positions. The H atoms were assigned as bonded to a planar (*sp*<sup>2</sup> hybridized) N atom, respectively with fixed bond angles and torsion angles, but the N—H bond distances were allowed to refine to account for asymmetry induced by charge and hydrogen bonding (AFIX 44 command). N—H distances refined to 0.83 (5) for N1—H1 and to 0.89 (2) for N3—H3, occupancies refined to 0.33 (2) for H1 and 0.67 (2) for H3. Methyl CH<sub>3</sub> were allowed to rotate but not to tip to best fit the experimental electron density. *U*<sub>iso</sub>(H) values were set to a multiple of *U*<sub>eq</sub>(C/N) with 1.5 for CH<sub>3</sub> and 1.2 for C—H and NH<sup>+</sup>, respectively.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> */ <i>U</i> <sub>eq</sub>	Occ. (<1)
C1	0.07995 (8)	0.11974 (12)	0.12505 (5)	0.02370 (17)	
H1	0.162507	0.154570	0.136425	0.028*	
C2	0.01650 (8)	0.02111 (12)	0.16550 (5)	0.02268 (16)	
H2	0.045537	−0.025178	0.209661	0.027*	
C3	−0.10216 (8)	0.08832 (10)	0.06876 (4)	0.01832 (14)	
C4	−0.20228 (9)	−0.08561 (12)	0.15402 (5)	0.02410 (17)	
H4A	−0.264761	−0.010298	0.167446	0.036*	
H4B	−0.172925	−0.150361	0.195187	0.036*	
H4C	−0.238614	−0.154975	0.116071	0.036*	
C5	−0.21283 (8)	0.09673 (13)	0.01670 (5)	0.02515 (18)	
H5A	−0.194381	0.162346	−0.023687	0.038*	
H5B	−0.281506	0.144135	0.039231	0.038*	
H5C	−0.235631	−0.010751	0.000206	0.038*	
C6	0.23459 (9)	0.40162 (12)	−0.00734 (5)	0.02566 (18)	
H6	0.285770	0.372447	0.034004	0.031*	
C7	0.26716 (8)	0.49589 (12)	−0.06067 (6)	0.02502 (18)	
H7	0.345007	0.545291	−0.063695	0.030*	
C8	0.07312 (8)	0.42021 (10)	−0.08640 (4)	0.01863 (14)	
C9	0.15832 (10)	0.59191 (13)	−0.17707 (5)	0.02847 (19)	
H9A	0.142896	0.516294	−0.216246	0.043*	
H9B	0.236534	0.647282	−0.181302	0.043*	
H9C	0.090972	0.669653	−0.178780	0.043*	
C10	−0.05084 (9)	0.40053 (13)	−0.12482 (5)	0.02596 (18)	
H10A	−0.090249	0.504931	−0.131824	0.039*	
H10B	−0.101453	0.332570	−0.097120	0.039*	
H10C	−0.042876	0.351054	−0.170954	0.039*	
C11	0.43346 (7)	0.00325 (9)	0.14618 (4)	0.01514 (13)	
C12	0.36079 (8)	−0.06738 (10)	0.19405 (4)	0.01852 (14)	
H12	0.326061	−0.004339	0.228696	0.022*	
C13	0.33919 (9)	−0.23035 (11)	0.19101 (5)	0.02475 (18)	
H13	0.289972	−0.278763	0.223810	0.030*	

C14	0.38933 (10)	-0.32262 (12)	0.14020 (6)	0.0293 (2)	
H14	0.375570	-0.434269	0.138722	0.035*	
C15	0.45951 (9)	-0.25157 (13)	0.09161 (6)	0.02817 (19)	
H15	0.492304	-0.314441	0.056220	0.034*	
C16	0.48217 (8)	-0.08834 (11)	0.09445 (5)	0.02151 (16)	
H16	0.530578	-0.039928	0.061247	0.026*	
N1	0.00522 (7)	0.16129 (10)	0.06471 (4)	0.02100 (14)	
H1N	0.0238 (11)	0.220 (3)	0.0325 (19)	0.025*	0.33 (2)
N2	-0.09869 (7)	0.00209 (9)	0.12923 (4)	0.01850 (13)	
N3	0.11314 (7)	0.35581 (10)	-0.02425 (4)	0.02125 (14)	
H3N	0.0690 (11)	0.2936 (16)	0.0021 (7)	0.026*	0.67 (2)
N4	0.16511 (7)	0.50600 (9)	-0.10967 (4)	0.02018 (14)	
O1	0.35734 (8)	0.28443 (9)	0.17511 (6)	0.0439 (2)	
O2	0.49875 (9)	0.26229 (11)	0.08516 (4)	0.0383 (2)	
O3	0.57130 (9)	0.21999 (10)	0.20780 (5)	0.0400 (2)	
S1	0.46799 (2)	0.20953 (2)	0.15392 (2)	0.01791 (6)	

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0187 (4)	0.0277 (4)	0.0242 (4)	-0.0014 (3)	-0.0009 (3)	0.0018 (3)
C2	0.0207 (4)	0.0263 (4)	0.0202 (4)	0.0008 (3)	-0.0024 (3)	0.0030 (3)
C3	0.0179 (3)	0.0208 (4)	0.0163 (3)	0.0012 (3)	0.0019 (3)	0.0019 (3)
C4	0.0218 (4)	0.0268 (4)	0.0244 (4)	-0.0017 (3)	0.0057 (3)	0.0059 (3)
C5	0.0206 (4)	0.0326 (5)	0.0214 (4)	-0.0007 (3)	-0.0025 (3)	0.0057 (3)
C6	0.0217 (4)	0.0257 (4)	0.0285 (4)	-0.0007 (3)	-0.0032 (3)	-0.0017 (3)
C7	0.0176 (4)	0.0236 (4)	0.0338 (5)	-0.0029 (3)	0.0020 (3)	-0.0033 (3)
C8	0.0182 (3)	0.0197 (3)	0.0183 (3)	-0.0019 (3)	0.0032 (3)	-0.0005 (3)
C9	0.0367 (5)	0.0263 (4)	0.0240 (4)	-0.0061 (4)	0.0108 (4)	0.0020 (3)
C10	0.0209 (4)	0.0326 (5)	0.0237 (4)	-0.0051 (3)	-0.0017 (3)	0.0037 (3)
C11	0.0138 (3)	0.0151 (3)	0.0160 (3)	-0.0013 (2)	-0.0009 (2)	0.0004 (2)
C12	0.0195 (3)	0.0185 (3)	0.0174 (3)	-0.0033 (3)	0.0012 (3)	0.0012 (3)
C13	0.0264 (4)	0.0195 (4)	0.0271 (4)	-0.0066 (3)	-0.0035 (3)	0.0064 (3)
C14	0.0310 (5)	0.0154 (4)	0.0388 (5)	0.0007 (3)	-0.0104 (4)	-0.0017 (3)
C15	0.0254 (4)	0.0259 (4)	0.0320 (5)	0.0068 (3)	-0.0036 (3)	-0.0108 (4)
C16	0.0171 (3)	0.0271 (4)	0.0203 (4)	0.0017 (3)	0.0017 (3)	-0.0031 (3)
N1	0.0185 (3)	0.0238 (3)	0.0208 (3)	-0.0010 (3)	0.0027 (2)	0.0026 (3)
N2	0.0179 (3)	0.0203 (3)	0.0174 (3)	0.0002 (2)	0.0017 (2)	0.0026 (2)
N3	0.0206 (3)	0.0230 (3)	0.0199 (3)	-0.0013 (3)	0.0008 (2)	0.0010 (3)
N4	0.0199 (3)	0.0193 (3)	0.0219 (3)	-0.0027 (2)	0.0051 (2)	-0.0011 (3)
O1	0.0321 (4)	0.0167 (3)	0.0868 (7)	-0.0008 (3)	0.0267 (5)	-0.0041 (4)
O2	0.0559 (5)	0.0311 (4)	0.0288 (4)	-0.0159 (4)	0.0089 (4)	0.0088 (3)
O3	0.0445 (5)	0.0265 (4)	0.0438 (5)	-0.0125 (3)	-0.0235 (4)	0.0020 (3)
S1	0.01652 (9)	0.01532 (9)	0.02171 (10)	-0.00380 (6)	0.00082 (7)	0.00194 (6)

*Geometric parameters (Å, °)*

C1—C2	1.3612 (13)	C9—H9A	0.9800
C1—N1	1.3845 (12)	C9—H9B	0.9800
C1—H1	0.9500	C9—H9C	0.9800
C2—N2	1.3809 (11)	C10—H10A	0.9800
C2—H2	0.9500	C10—H10B	0.9800
C3—N1	1.3283 (11)	C10—H10C	0.9800
C3—N2	1.3541 (11)	C11—C16	1.3910 (12)
C3—C5	1.4848 (12)	C11—C12	1.3921 (11)
C4—N2	1.4613 (11)	C11—S1	1.7767 (8)
C4—H4A	0.9800	C12—C13	1.3897 (12)
C4—H4B	0.9800	C12—H12	0.9500
C4—H4C	0.9800	C13—C14	1.3883 (15)
C5—H5A	0.9800	C13—H13	0.9500
C5—H5B	0.9800	C14—C15	1.3866 (16)
C5—H5C	0.9800	C14—H14	0.9500
C6—C7	1.3580 (14)	C15—C16	1.3937 (14)
C6—N3	1.3847 (12)	C15—H15	0.9500
C6—H6	0.9500	C16—H16	0.9500
C7—N4	1.3815 (12)	N1—H1N	0.83 (5)
C7—H7	0.9500	N3—H3N	0.89 (2)
C8—N3	1.3322 (11)	O1—S1	1.4489 (8)
C8—N4	1.3418 (11)	O2—S1	1.4465 (8)
C8—C10	1.4805 (12)	O3—S1	1.4484 (8)
C9—N4	1.4639 (12)		
C2—C1—N1	109.27 (8)	C8—C10—H10C	109.5
C2—C1—H1	125.4	H10A—C10—H10C	109.5
N1—C1—H1	125.4	H10B—C10—H10C	109.5
C1—C2—N2	105.94 (8)	C16—C11—C12	120.15 (8)
C1—C2—H2	127.0	C16—C11—S1	120.42 (6)
N2—C2—H2	127.0	C12—C11—S1	119.39 (6)
N1—C3—N2	110.00 (7)	C13—C12—C11	119.83 (8)
N1—C3—C5	127.01 (8)	C13—C12—H12	120.1
N2—C3—C5	122.99 (8)	C11—C12—H12	120.1
N2—C4—H4A	109.5	C14—C13—C12	120.20 (9)
N2—C4—H4B	109.5	C14—C13—H13	119.9
H4A—C4—H4B	109.5	C12—C13—H13	119.9
N2—C4—H4C	109.5	C15—C14—C13	119.89 (9)
H4A—C4—H4C	109.5	C15—C14—H14	120.1
H4B—C4—H4C	109.5	C13—C14—H14	120.1
C3—C5—H5A	109.5	C14—C15—C16	120.31 (9)
C3—C5—H5B	109.5	C14—C15—H15	119.8
H5A—C5—H5B	109.5	C16—C15—H15	119.8
C3—C5—H5C	109.5	C11—C16—C15	119.60 (9)
H5A—C5—H5C	109.5	C11—C16—H16	120.2
H5B—C5—H5C	109.5	C15—C16—H16	120.2

C7—C6—N3	107.48 (8)	C3—N1—C1	106.66 (8)
C7—C6—H6	126.3	C3—N1—H1N	126.7
N3—C6—H6	126.3	C1—N1—H1N	126.7
C6—C7—N4	106.69 (8)	C3—N2—C2	108.13 (7)
C6—C7—H7	126.7	C3—N2—C4	125.59 (7)
N4—C7—H7	126.7	C2—N2—C4	126.12 (7)
N3—C8—N4	108.53 (8)	C8—N3—C6	108.47 (8)
N3—C8—C10	126.61 (8)	C8—N3—H3N	125.8
N4—C8—C10	124.85 (8)	C6—N3—H3N	125.8
N4—C9—H9A	109.5	C8—N4—C7	108.83 (8)
N4—C9—H9B	109.5	C8—N4—C9	125.08 (8)
H9A—C9—H9B	109.5	C7—N4—C9	126.06 (8)
N4—C9—H9C	109.5	O2—S1—O3	112.77 (6)
H9A—C9—H9C	109.5	O2—S1—O1	112.73 (6)
H9B—C9—H9C	109.5	O3—S1—O1	112.82 (7)
C8—C10—H10A	109.5	O2—S1—C11	106.84 (4)
C8—C10—H10B	109.5	O3—S1—C11	105.15 (4)
H10A—C10—H10B	109.5	O1—S1—C11	105.78 (4)
N1—C1—C2—N2	0.06 (11)	C1—C2—N2—C3	-0.06 (10)
N3—C6—C7—N4	-0.20 (11)	C1—C2—N2—C4	-175.75 (9)
C16—C11—C12—C13	1.40 (12)	N4—C8—N3—C6	-0.12 (10)
S1—C11—C12—C13	-176.27 (7)	C10—C8—N3—C6	179.13 (9)
C11—C12—C13—C14	-0.33 (13)	C7—C6—N3—C8	0.20 (11)
C12—C13—C14—C15	-1.04 (14)	N3—C8—N4—C7	0.00 (10)
C13—C14—C15—C16	1.35 (15)	C10—C8—N4—C7	-179.28 (9)
C12—C11—C16—C15	-1.09 (12)	N3—C8—N4—C9	178.37 (8)
S1—C11—C16—C15	176.55 (7)	C10—C8—N4—C9	-0.91 (14)
C14—C15—C16—C11	-0.28 (14)	C6—C7—N4—C8	0.13 (10)
N2—C3—N1—C1	0.00 (10)	C6—C7—N4—C9	-178.22 (9)
C5—C3—N1—C1	179.55 (9)	C16—C11—S1—O2	24.77 (8)
C2—C1—N1—C3	-0.04 (11)	C12—C11—S1—O2	-157.57 (7)
N1—C3—N2—C2	0.03 (10)	C16—C11—S1—O3	-95.30 (8)
C5—C3—N2—C2	-179.54 (9)	C12—C11—S1—O3	82.36 (8)
N1—C3—N2—C4	175.76 (8)	C16—C11—S1—O1	145.10 (8)
C5—C3—N2—C4	-3.81 (14)	C12—C11—S1—O1	-37.24 (9)

## 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—H1N...N3	0.83	1.90	2.6970 (11)	163
N3—H3N...N1	0.89	1.81	2.6970 (11)	170
C1—H1...O1	0.95	2.43	3.3741 (13)	170
C4—H4B...O3 <sup>i</sup>	0.98	2.33	3.2956 (12)	170
C6—H6...O2	0.95	2.60	3.4288 (14)	146
C7—H7...O2 <sup>ii</sup>	0.95	2.41	3.3254 (12)	162
C9—H9A...O3 <sup>iii</sup>	0.98	2.53	3.4846 (14)	164
C9—H9B...O3 <sup>ii</sup>	0.98	2.46	3.4381 (14)	173



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C13—H13···O1 <sup>i</sup>	0.95	2.67	3.4738 (14)	143
C14—H14···O1 <sup>iv</sup>	0.95	2.48	3.3920 (13)	162

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Symmetry codes: (i)  $-x+1/2, y-1/2, -z+1/2$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $x-1/2, -y+1/2, z-1/2$ ; (iv)  $x, y-1, z$ .