

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-(4-Nitrobenzyl)pyridinium 3-carboxy-4-hydroxybenzenesulfonate

Graham Smith* and Urs D. Wermuth

Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia
Correspondence e-mail: g.smith@qut.edu.au

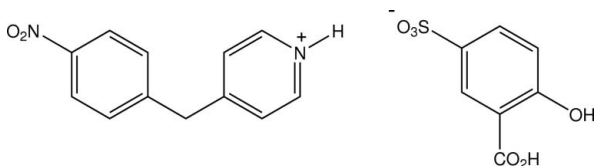
Received 20 December 2012; accepted 2 January 2013

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.071; wR factor = 0.173; data-to-parameter ratio = 13.5.

In the title salt, $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_6\text{S}^-$, the dihedral angle between the benzene and pyridine rings in the 4-(4-nitrobenzyl)pyridinium cation is $82.7(2)^\circ$. Within the anion there is an intramolecular hydroxy- $\text{O}-\text{H} \cdots \text{O}(\text{carboxylic acid})$ bond. In the crystal, the cation forms a single $\text{N}^+-\text{H} \cdots \text{O}_{\text{sulfonate}}$ hydrogen bond with the anion. These cation-anion pairs interact through duplex anion carboxylic acid $\text{O}-\text{H} \cdots \text{O}_{\text{sulfonate}}$ hydrogen bonds, giving a centrosymmetric cyclic association [graph set $R_2^2(16)$]. The crystals studied were non-merohedrally twinned.

Related literature

For data on 4-(4-nitrobenzyl)pyridine adduct and salt structures, see: Smith *et al.* (1997); Smith & Wermuth (2010). For examples of the structures of salts of 5-sulfosalicylic acid, see: Raj *et al.* (2003); Smith *et al.* (2004). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_6\text{S}^-$
 $M_r = 432.41$
Monoclinic, $P2_1/c$
 $a = 7.4154(7)$ Å

$b = 12.8896(10)$ Å
 $c = 19.649(2)$ Å
 $\beta = 92.848(9)^\circ$
 $V = 1875.8(3)$ Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.23$ mm⁻¹

$T = 200$ K
 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
 $T_{\text{min}} = 0.916$, $T_{\text{max}} = 0.980$
14534 measured reflections
3671 independent reflections
2631 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.173$
 $S = 1.21$
3671 reflections
272 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

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

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--|-------|--------------|--------------|----------------|
| $\text{N1}-\text{H1} \cdots \text{O51A}$ | 0.86 | 1.88 | 2.732 (5) | 172 |
| $\text{O2A}-\text{H2A} \cdots \text{O12A}$ | 0.95 | 1.70 | 2.613 (5) | 159 |
| $\text{O11A}-\text{H11A} \cdots \text{O53A}^i$ | 0.94 | 1.65 | 2.583 (4) | 172 |

Symmetry code: (i) $-x + 2, -y, -z + 1$.

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) within *WinGX* (Farrugia, 2012); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The authors acknowledge financial support from the Australian Research Council, the Science and Engineering Faculty and the University Library, Queensland University of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2470).

References

- Agilent (2012). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.
Altomare, A., Casciaro, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Raj, S. B., Sethuraman, V., Francis, S., Hemamalini, M., Muthiah, P. T., Bocelli, G., Cantoni, A., Rychlewska, U. & Warzajtis, B. (2003). *CrysEngComm*, **5**, 70–76.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1997). *J. Chem. Crystallogr.* **27**, 307–317.
Smith, G. & Wermuth, U. D. (2010). *Acta Cryst.* **E66**, o1173.
Smith, G., Wermuth, U. D. & White, J. M. (2004). *Acta Cryst.* **C60**, o575–o581.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.

supporting information

Acta Cryst. (2013). E69, o206 [doi:10.1107/S1600536813000093]

4-(4-Nitrobenzyl)pyridinium 3-carboxy-4-hydroxybenzenesulfonate

Graham Smith and Urs D. Wermuth

S1. Comment

The Lewis base 4-(4-nitrobenzyl)pyridine (NBPY) is an analogue of 2-(2,4-dinitrobenzyl)pyridine (DNBPY) which is significant because of its unusual photochromic behaviour in the solid state, although NBPY does not possess such properties. The structure of NBPY is not known but both the structures of a 2:1 co-crystal adduct with 4-aminobenzoic acid (Smith *et al.*, 1997) and a 5-nitrosalicylate salt (Smith & Wermuth, 2010) have been reported. Our reaction of NBPY with 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid = 5-SSA) gave the title compound, $C_{12}H_{11}N_2O_2^+ C_7H_5O_6S^-$, the structure of which is reported herein. The structures of a number of 1:1 salts of 5-SSA are known (Raj *et al.*, 2003; Smith *et al.*, 2004).

With the title compound (Fig. 1), the dihedral angle between the phenyl and pyridine rings in the 4-(4-nitrobenzyl)pyridinium cation is $82.7(2)^\circ$ and this forms a single $N^+—H\cdots O_{\text{sulfonate}}$ hydrogen bond with the anion. These cation–anion pairs inter-associate through duplex anion carboxylic acid $O—H\cdots O_{\text{sulfonate}}$ hydrogen bonds (Table 1, Fig. 2) giving a centrosymmetric cyclic motif [graph set $R^2_2(16)$ (Etter *et al.*, 1990)]. Crystals of the compound are non-merohedrally twinned [BASF factor 0.3201 (Sheldrick, 2008); see *Refinement* section].

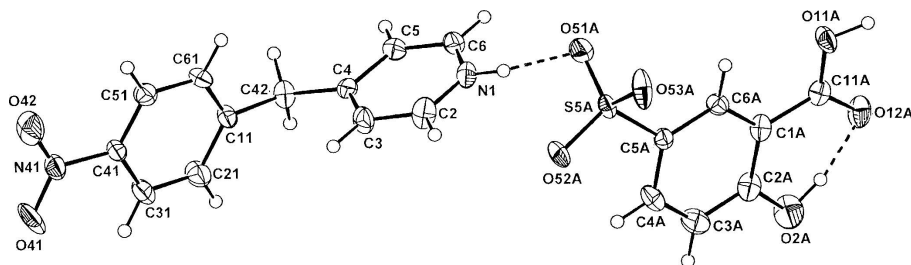
In the 5-SSA monoanion, the usual intramolecular phenol $O—H\cdots O_{\text{carboxyl}}$ hydrogen bond [2.613 (5) Å] is present, essentially maintaining coplanarity of the carboxylic acid group and the benzene ring [torsion angle C2A—C1A—C11A—O11A, $-176.6(4)^\circ$] (Raj *et al.*, 2003; Smith *et al.*, 2004).

S2. Experimental

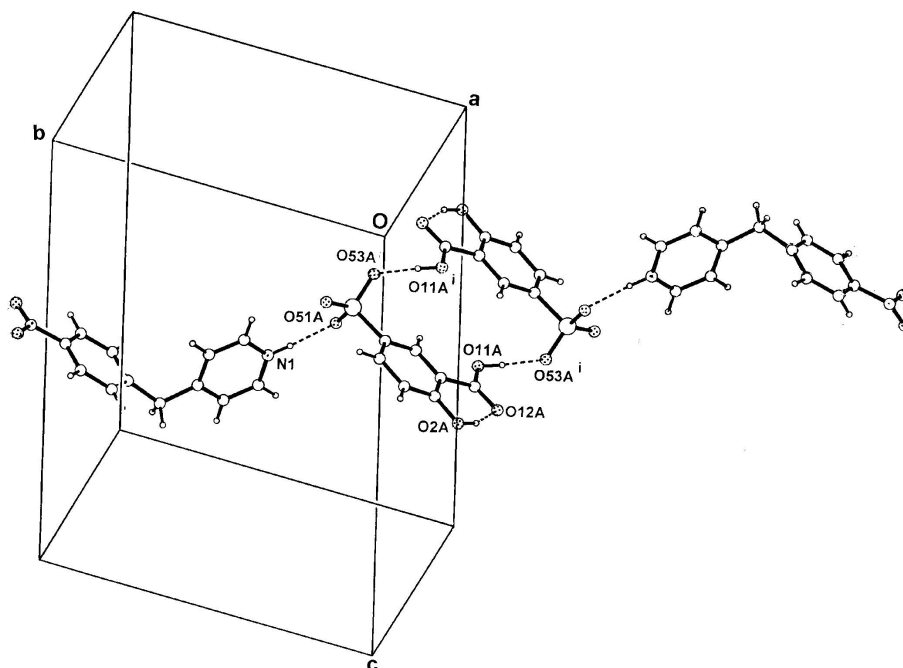
The title compound was synthesized by heating together under reflux for 10 minutes, 1 mmol quantities of 4-(4-nitrobenzyl)pyridine with 5-sulfosalicylic acid in 50 ml of 50% ethanol–water. After concentration to *ca.* 30 ml, partial room temperature evaporation of the hot-filtered solution gave colourless crystals from which a block section was cleaved for the X-ray analysis.

S3. Refinement

Hydrogen atoms involved in hydrogen-bonding interactions were located by difference methods but their positional and isotropic displacement parameters were allowed to ride in the refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$. Other H atoms were included in the refinement at calculated positions [C—H = 0.93 Å (aromatic) and 0.97 Å (aliphatic) and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$], also using a riding-model approximation. The crystal was found to be non-merohedrally twinned [Twin Rot Mat [PLATON (Spek, 2009)]: matrix, -1 0 0, 0 - 1 0, 0.263 0 1] and the data generated were used in the final refinement (refined BASF = 0.3201).

**Figure 1**

Molecular configuration and atom naming scheme for the hydrogen-bonded NBPY cation and 5-SSA monoanion species in the title salt. Hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 40% probability level.

**Figure 2**

A perspective view of the crystal packing in the unit cell showing the centrosymmetric anion-associated hydrogen-bonded cation-anion pairs. For symmetry code (i), see Table 1.

4-(4-Nitrobenzyl)pyridinium 3-carboxy-4-hydroxybenzenesulfonate

Crystal data

$C_{12}H_{11}N_2O_2^+ \cdot C_7H_5O_6S^-$

$M_r = 432.41$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 7.4154$ (7) Å

$b = 12.8896$ (10) Å

$c = 19.649$ (2) Å

$\beta = 92.848$ (9)°

$V = 1875.8$ (3) Å³

$Z = 4$

$F(000) = 896$

$D_x = 1.531$ Mg m⁻³

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

Cell parameters from 3757 reflections

$\theta = 3.2$ – 28.8 °

$\mu = 0.23$ mm⁻¹

$T = 200$ K

Block, colourless

$0.25 \times 0.20 \times 0.15$ mm

Data collection

Oxford Diffraction Gemini-S CCD-detector
diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.077 pixels mm⁻¹
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Agilent, 2012)
 $T_{\min} = 0.916$, $T_{\max} = 0.980$

14534 measured reflections
3671 independent reflections
2631 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.2^\circ$
 $h = -9 \rightarrow 9$
 $k = -15 \rightarrow 15$
 $l = 0 \rightarrow 24$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.173$
 $S = 1.21$
3671 reflections
272 parameters
0 restraints
0 constraints
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
 $w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 2.5904P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|-------------|--------------|----------------------------------|
| O41 | 0.5308 (6) | 1.2075 (3) | 0.6714 (2) | 0.0669 (15) |
| O42 | 0.4378 (6) | 1.1939 (3) | 0.5666 (2) | 0.0580 (16) |
| N1 | 0.6089 (5) | 0.4772 (3) | 0.58094 (19) | 0.0343 (14) |
| N41 | 0.4750 (5) | 1.1565 (3) | 0.6224 (2) | 0.0374 (14) |
| C2 | 0.6921 (7) | 0.5677 (4) | 0.5906 (3) | 0.0433 (19) |
| C3 | 0.6005 (7) | 0.6507 (4) | 0.6162 (3) | 0.0363 (16) |
| C4 | 0.4226 (6) | 0.6405 (3) | 0.6324 (2) | 0.0265 (14) |
| C5 | 0.3420 (6) | 0.5439 (3) | 0.6213 (2) | 0.0332 (16) |
| C6 | 0.4369 (7) | 0.4631 (3) | 0.5959 (2) | 0.0347 (16) |
| C11 | 0.3719 (6) | 0.8367 (3) | 0.6512 (2) | 0.0304 (16) |
| C21 | 0.4350 (8) | 0.8981 (4) | 0.7051 (2) | 0.0439 (19) |
| C31 | 0.4738 (7) | 1.0020 (4) | 0.6955 (3) | 0.0447 (19) |
| C41 | 0.4452 (6) | 1.0441 (3) | 0.6322 (2) | 0.0294 (16) |
| C42 | 0.3137 (7) | 0.7262 (3) | 0.6619 (2) | 0.0351 (16) |
| C51 | 0.3888 (6) | 0.9853 (4) | 0.5774 (2) | 0.0328 (16) |
| C61 | 0.3547 (6) | 0.8809 (3) | 0.5871 (2) | 0.0305 (14) |
| S5A | 0.96726 (16) | 0.31180 (8) | 0.53828 (6) | 0.0283 (3) |
| O2A | 1.0084 (6) | -0.0013 (3) | 0.75787 (17) | 0.0573 (14) |
| O11A | 0.8687 (5) | -0.0882 (2) | 0.55774 (16) | 0.0372 (10) |
| O12A | 0.9140 (5) | -0.1398 (2) | 0.66576 (17) | 0.0427 (11) |
| O51A | 0.7756 (5) | 0.3169 (2) | 0.51826 (16) | 0.0385 (11) |
| O52A | 1.0352 (5) | 0.4070 (2) | 0.56822 (18) | 0.0433 (11) |
| O53A | 1.0709 (5) | 0.2754 (2) | 0.48221 (18) | 0.0503 (13) |
| C1A | 0.9474 (6) | 0.0393 (3) | 0.6394 (2) | 0.0317 (16) |

| | | | | |
|------|------------|-------------|------------|-------------|
| C2A | 1.0008 (7) | 0.0680 (4) | 0.7061 (2) | 0.0363 (16) |
| C3A | 1.0483 (7) | 0.1698 (4) | 0.7204 (2) | 0.0443 (17) |
| C4A | 1.0432 (7) | 0.2439 (4) | 0.6695 (2) | 0.0361 (17) |
| C5A | 0.9863 (6) | 0.2161 (3) | 0.6031 (2) | 0.0250 (12) |
| C6A | 0.9407 (6) | 0.1142 (3) | 0.5884 (2) | 0.0273 (14) |
| C11A | 0.9080 (6) | -0.0709 (3) | 0.6227 (2) | 0.0304 (14) |
| H1 | 0.66760 | 0.42610 | 0.56460 | 0.0410* |
| H2 | 0.81240 | 0.57490 | 0.58020 | 0.0520* |
| H3 | 0.65890 | 0.71410 | 0.62250 | 0.0440* |
| H5 | 0.22190 | 0.53430 | 0.63130 | 0.0400* |
| H6 | 0.38210 | 0.39880 | 0.58900 | 0.0420* |
| H21 | 0.45160 | 0.86920 | 0.74840 | 0.0520* |
| H31 | 0.51860 | 1.04250 | 0.73170 | 0.0540* |
| H51 | 0.37360 | 1.01480 | 0.53430 | 0.0390* |
| H61 | 0.31950 | 0.83990 | 0.54990 | 0.0370* |
| H421 | 0.31140 | 0.71450 | 0.71060 | 0.0420* |
| H422 | 0.19060 | 0.71940 | 0.64330 | 0.0420* |
| H2A | 0.97480 | -0.06270 | 0.73320 | 0.0860* |
| H3A | 1.08390 | 0.18860 | 0.76480 | 0.0530* |
| H4A | 1.07740 | 0.31190 | 0.67930 | 0.0430* |
| H6A | 0.90540 | 0.09560 | 0.54390 | 0.0320* |
| H11A | 0.88000 | -0.15700 | 0.54300 | 0.0560* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|------|------------|-------------|-------------|--------------|--------------|--------------|
| O41 | 0.098 (3) | 0.0271 (19) | 0.074 (3) | -0.016 (2) | -0.012 (3) | -0.020 (2) |
| O42 | 0.082 (3) | 0.033 (2) | 0.059 (3) | -0.008 (2) | 0.004 (2) | 0.0134 (19) |
| N1 | 0.040 (3) | 0.027 (2) | 0.036 (2) | 0.0075 (19) | 0.0044 (18) | 0.0012 (18) |
| N41 | 0.034 (2) | 0.024 (2) | 0.054 (3) | -0.0013 (18) | -0.001 (2) | -0.006 (2) |
| C2 | 0.032 (3) | 0.034 (3) | 0.065 (4) | 0.000 (2) | 0.013 (3) | 0.008 (3) |
| C3 | 0.039 (3) | 0.020 (2) | 0.050 (3) | -0.004 (2) | 0.004 (2) | 0.003 (2) |
| C4 | 0.033 (3) | 0.021 (2) | 0.025 (2) | -0.002 (2) | -0.0044 (19) | 0.0075 (18) |
| C5 | 0.030 (3) | 0.031 (2) | 0.038 (3) | -0.002 (2) | -0.003 (2) | -0.003 (2) |
| C6 | 0.043 (3) | 0.023 (2) | 0.037 (3) | -0.003 (2) | -0.008 (2) | 0.001 (2) |
| C11 | 0.033 (3) | 0.023 (2) | 0.035 (3) | 0.002 (2) | 0.001 (2) | -0.007 (2) |
| C21 | 0.069 (4) | 0.035 (3) | 0.027 (3) | -0.002 (3) | -0.004 (2) | 0.000 (2) |
| C31 | 0.066 (4) | 0.028 (3) | 0.039 (3) | 0.000 (3) | -0.009 (3) | -0.011 (2) |
| C41 | 0.029 (3) | 0.023 (2) | 0.036 (3) | 0.001 (2) | -0.001 (2) | -0.008 (2) |
| C42 | 0.040 (3) | 0.026 (2) | 0.040 (3) | 0.003 (2) | 0.008 (2) | 0.001 (2) |
| C51 | 0.036 (3) | 0.031 (2) | 0.031 (3) | -0.002 (2) | -0.001 (2) | 0.001 (2) |
| C61 | 0.035 (3) | 0.030 (2) | 0.026 (2) | -0.006 (2) | -0.002 (2) | -0.007 (2) |
| S5A | 0.0326 (6) | 0.0160 (5) | 0.0364 (6) | -0.0023 (5) | 0.0040 (5) | -0.0030 (5) |
| O2A | 0.093 (3) | 0.051 (2) | 0.0285 (19) | 0.004 (2) | 0.0092 (19) | 0.0112 (18) |
| O11A | 0.059 (2) | 0.0190 (15) | 0.0336 (18) | -0.0051 (16) | 0.0011 (16) | 0.0005 (14) |
| O12A | 0.059 (2) | 0.0300 (18) | 0.040 (2) | 0.0037 (18) | 0.0116 (17) | 0.0138 (16) |
| O51A | 0.046 (2) | 0.0291 (17) | 0.0398 (19) | -0.0026 (17) | -0.0037 (15) | -0.0011 (15) |
| O52A | 0.049 (2) | 0.0192 (16) | 0.061 (2) | -0.0087 (16) | -0.0056 (18) | -0.0087 (16) |

| | | | | | | |
|------|-----------|-------------|-----------|--------------|-------------|--------------|
| O53A | 0.079 (3) | 0.0230 (16) | 0.052 (2) | 0.0096 (18) | 0.036 (2) | 0.0085 (16) |
| C1A | 0.034 (3) | 0.028 (2) | 0.034 (3) | 0.003 (2) | 0.011 (2) | 0.005 (2) |
| C2A | 0.047 (3) | 0.037 (3) | 0.026 (2) | 0.010 (2) | 0.013 (2) | 0.004 (2) |
| C3A | 0.057 (3) | 0.049 (3) | 0.027 (3) | 0.002 (3) | 0.002 (2) | -0.011 (2) |
| C4A | 0.039 (3) | 0.031 (3) | 0.039 (3) | -0.004 (2) | 0.009 (2) | -0.013 (2) |
| C5A | 0.022 (2) | 0.021 (2) | 0.032 (2) | -0.0002 (18) | 0.0023 (19) | -0.0011 (18) |
| C6A | 0.031 (3) | 0.028 (2) | 0.023 (2) | -0.002 (2) | 0.0027 (19) | -0.0013 (19) |
| C11A | 0.026 (2) | 0.031 (2) | 0.035 (3) | 0.002 (2) | 0.009 (2) | 0.005 (2) |

Geometric parameters (Å, °)

| | | | |
|----------------|-------------|---------------|-----------|
| S5A—C5A | 1.774 (4) | C31—C41 | 1.364 (7) |
| S5A—O53A | 1.452 (4) | C41—C51 | 1.365 (6) |
| S5A—O51A | 1.457 (4) | C51—C61 | 1.384 (6) |
| S5A—O52A | 1.441 (3) | C2—H2 | 0.9300 |
| O41—N41 | 1.221 (6) | C3—H3 | 0.9300 |
| O42—N41 | 1.217 (6) | C5—H5 | 0.9300 |
| O2A—C2A | 1.353 (6) | C6—H6 | 0.9300 |
| O11A—C11A | 1.314 (5) | C21—H21 | 0.9300 |
| O12A—C11A | 1.226 (5) | C31—H31 | 0.9300 |
| O2A—H2A | 0.9500 | C42—H422 | 0.9700 |
| O11A—H11A | 0.9400 | C42—H421 | 0.9700 |
| N1—C6 | 1.336 (6) | C51—H51 | 0.9300 |
| N1—C2 | 1.329 (6) | C61—H61 | 0.9300 |
| N41—C41 | 1.480 (5) | C1A—C11A | 1.484 (6) |
| N1—H1 | 0.8600 | C1A—C2A | 1.400 (6) |
| C2—C3 | 1.376 (7) | C1A—C6A | 1.391 (6) |
| C3—C4 | 1.379 (7) | C2A—C3A | 1.384 (7) |
| C4—C5 | 1.394 (6) | C3A—C4A | 1.382 (6) |
| C4—C42 | 1.502 (6) | C4A—C5A | 1.398 (6) |
| C5—C6 | 1.365 (6) | C5A—C6A | 1.383 (6) |
| C11—C21 | 1.385 (6) | C3A—H3A | 0.9300 |
| C11—C42 | 1.506 (6) | C4A—H4A | 0.9300 |
| C11—C61 | 1.383 (6) | C6A—H6A | 0.9300 |
| C21—C31 | 1.385 (7) | | |
| O51A—S5A—O53A | 110.8 (2) | C6—C5—H5 | 119.00 |
| O51A—S5A—C5A | 105.49 (19) | N1—C6—H6 | 120.00 |
| O52A—S5A—O53A | 113.4 (2) | C5—C6—H6 | 120.00 |
| O52A—S5A—C5A | 106.6 (2) | C11—C21—H21 | 120.00 |
| O53A—S5A—C5A | 107.09 (19) | C31—C21—H21 | 119.00 |
| O51A—S5A—O52A | 112.85 (19) | C21—C31—H31 | 120.00 |
| C2A—O2A—H2A | 100.00 | C41—C31—H31 | 120.00 |
| C11A—O11A—H11A | 116.00 | C4—C42—H422 | 108.00 |
| C2—N1—C6 | 122.0 (4) | C11—C42—H421 | 108.00 |
| O41—N41—O42 | 123.4 (4) | C11—C42—H422 | 108.00 |
| O42—N41—C41 | 118.5 (4) | H421—C42—H422 | 107.00 |
| O41—N41—C41 | 118.1 (4) | C4—C42—H421 | 108.00 |

| | | | |
|------------------|------------|-------------------|------------|
| C6—N1—H1 | 119.00 | C41—C51—H51 | 121.00 |
| C2—N1—H1 | 119.00 | C61—C51—H51 | 121.00 |
| N1—C2—C3 | 120.1 (5) | C11—C61—H61 | 119.00 |
| C2—C3—C4 | 120.4 (5) | C51—C61—H61 | 119.00 |
| C5—C4—C42 | 118.9 (4) | C6A—C1A—C11A | 120.4 (4) |
| C3—C4—C5 | 117.2 (4) | C2A—C1A—C11A | 120.2 (4) |
| C3—C4—C42 | 123.9 (4) | C2A—C1A—C6A | 119.3 (4) |
| C4—C5—C6 | 120.9 (4) | O2A—C2A—C3A | 118.2 (4) |
| N1—C6—C5 | 119.5 (4) | O2A—C2A—C1A | 121.9 (4) |
| C21—C11—C42 | 121.5 (4) | C1A—C2A—C3A | 119.9 (4) |
| C21—C11—C61 | 118.3 (4) | C2A—C3A—C4A | 120.7 (4) |
| C42—C11—C61 | 120.2 (4) | C3A—C4A—C5A | 119.6 (4) |
| C11—C21—C31 | 120.9 (4) | C4A—C5A—C6A | 119.8 (4) |
| C21—C31—C41 | 119.0 (5) | S5A—C5A—C4A | 120.1 (3) |
| N41—C41—C31 | 119.4 (4) | S5A—C5A—C6A | 120.0 (3) |
| N41—C41—C51 | 118.9 (4) | C1A—C6A—C5A | 120.6 (4) |
| C31—C41—C51 | 121.7 (4) | O12A—C11A—C1A | 122.8 (4) |
| C4—C42—C11 | 118.6 (4) | O11A—C11A—O12A | 123.1 (4) |
| C41—C51—C61 | 118.8 (4) | O11A—C11A—C1A | 114.1 (3) |
| C11—C61—C51 | 121.1 (4) | C2A—C3A—H3A | 120.00 |
| N1—C2—H2 | 120.00 | C4A—C3A—H3A | 120.00 |
| C3—C2—H2 | 120.00 | C3A—C4A—H4A | 120.00 |
| C4—C3—H3 | 120.00 | C5A—C4A—H4A | 120.00 |
| C2—C3—H3 | 120.00 | C1A—C6A—H6A | 120.00 |
| C4—C5—H5 | 120.00 | C5A—C6A—H6A | 120.00 |
| O53A—S5A—C5A—C6A | -54.6 (4) | C42—C11—C61—C51 | 172.9 (4) |
| O52A—S5A—C5A—C4A | 5.3 (4) | C11—C21—C31—C41 | 1.4 (8) |
| O53A—S5A—C5A—C4A | 126.9 (4) | C21—C31—C41—N41 | 176.1 (5) |
| O51A—S5A—C5A—C4A | -114.9 (4) | C21—C31—C41—C51 | -3.6 (8) |
| O52A—S5A—C5A—C6A | -176.3 (4) | C31—C41—C51—C61 | 2.0 (7) |
| O51A—S5A—C5A—C6A | 63.5 (4) | N41—C41—C51—C61 | -177.7 (4) |
| C6—N1—C2—C3 | -0.6 (8) | C41—C51—C61—C11 | 1.9 (7) |
| C2—N1—C6—C5 | 0.6 (7) | C2A—C1A—C11A—O11A | -176.6 (4) |
| O41—N41—C41—C31 | 2.5 (6) | C2A—C1A—C11A—O12A | 2.6 (7) |
| O42—N41—C41—C51 | 4.3 (6) | C6A—C1A—C11A—O11A | 0.1 (6) |
| O41—N41—C41—C51 | -177.8 (4) | C6A—C1A—C11A—O12A | 179.2 (4) |
| O42—N41—C41—C31 | -175.4 (5) | C11A—C1A—C2A—O2A | -3.8 (7) |
| N1—C2—C3—C4 | 0.4 (8) | C11A—C1A—C2A—C3A | 175.9 (4) |
| C2—C3—C4—C42 | 178.7 (5) | C2A—C1A—C6A—C5A | 0.0 (7) |
| C2—C3—C4—C5 | -0.4 (7) | C11A—C1A—C6A—C5A | -176.7 (4) |
| C3—C4—C5—C6 | 0.5 (6) | C6A—C1A—C2A—O2A | 179.4 (5) |
| C42—C4—C5—C6 | -178.6 (4) | C6A—C1A—C2A—C3A | -0.8 (7) |
| C3—C4—C42—C11 | 22.4 (6) | O2A—C2A—C3A—C4A | 180.0 (5) |
| C5—C4—C42—C11 | -158.6 (4) | C1A—C2A—C3A—C4A | 0.2 (8) |
| C4—C5—C6—N1 | -0.6 (6) | C2A—C3A—C4A—C5A | 1.2 (8) |
| C61—C11—C42—C4 | 69.8 (6) | C3A—C4A—C5A—C6A | -1.9 (7) |
| C21—C11—C61—C51 | -3.9 (7) | C3A—C4A—C5A—S5A | 176.5 (4) |

| | | | |
|-----------------|------------|-----------------|------------|
| C21—C11—C42—C4 | -113.5 (5) | S5A—C5A—C6A—C1A | -177.2 (3) |
| C42—C11—C21—C31 | -174.6 (5) | C4A—C5A—C6A—C1A | 1.3 (7) |
| C61—C11—C21—C31 | 2.3 (8) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| N1—H1 \cdots O51A | 0.86 | 1.88 | 2.732 (5) | 172 |
| O2A—H2A \cdots O12A | 0.95 | 1.70 | 2.613 (5) | 159 |
| O11A—H11A \cdots O53A ⁱ | 0.94 | 1.65 | 2.583 (4) | 172 |
| C2—H2 \cdots O53A ⁱⁱ | 0.93 | 2.47 | 3.078 (6) | 123 |
| C3A—H3A \cdots O12A ⁱⁱⁱ | 0.93 | 2.60 | 3.323 (6) | 135 |
| C4A—H4A \cdots O52A | 0.93 | 2.51 | 2.893 (6) | 105 |
| C5—H5 \cdots O52A ^{iv} | 0.93 | 2.44 | 3.024 (5) | 120 |
| C6—H6 \cdots O52A ^{iv} | 0.93 | 2.59 | 3.087 (6) | 114 |
| C6A—H6A \cdots O11A | 0.93 | 2.40 | 2.724 (5) | 100 |
| C61—H61 \cdots O51A ^v | 0.93 | 2.51 | 3.394 (5) | 160 |
| C42—H421 \cdots O41 ^{vi} | 0.97 | 2.55 | 3.427 (6) | 151 |

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