4-(4-Aminophenylsulfonyl)anilinium toluene-4-sulfonate

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4-(4-Aminophenylsulfonyl)anilinium toluene-4-sulfonate

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Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.061; wR factor = 0.161; data-to-parameter ratio = 14.4.

In the title p-toluenesulfonate salt of the drug dapsone, C₁₂H₁₃N₂O₂S⁺·C₇H₇O₃S⁻, the dihedral angle between the two aromatic rings of the dapsone monocation is 70.19 (17)° and those between these rings and that of the p-toluenesulfonate anion are 72.34 (17)° and 46.43 (17)°. All amine and aminium H atoms are involved in intermolecular N—H···O hydrogen-bonding associations with sulfonyl O-atom acceptors as well as one of the sulfonyl O atoms, giving a three-dimensional structure.

Related literature

For drug applications of dapsone, see: Wilson et al. (1991). For the structures of dapsone solvates, see: Kus’mina et al. (1981); Lemmer et al. (2012). For the structures of adducts and a salt of dapsone, see: Smith & Wermuth (2012a,b, 2013).

Experimental

Crystal data

C₁₂H₁₃N₂O₂S⁺·C₇H₇O₃S⁻  V = 1856.6 (4) Å³
M_r = 420.49  Z = 4
Monoclinic, P2₁/n  Mo Kα radiation
a = 9.5916 (9) Å  μ = 0.32 mm⁻¹
b = 25.147 (3) Å  T = 200 K
c = 12.4506 (15) Å  0.25 × 0.12 × 0.12 mm
β = 94.908 (11)°

Data collection

Oxford Diffraction Gemini-S CCD-detector diffractometer
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2013)
T_min = 0.935, T_max = 0.980
3650 independent reflections
3650 reflections with I > 2σ(I)
R_int = 0.046

Refinement

R[F² > 2σ(F²)] = 0.061
wR(F²) = 0.161
S = 1.02
253 parameters
H-atom parameters constrained
Δρ_max = 0.33 e Å⁻³
Δρ_min = −0.39 e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A  D—H  H···A  D···A  D—H···A
N4—H41···O13A  0.86  1.91  2.759 (4)  165
N4—H42···O11B  0.83  2.24  3.008 (4)  153
N4—H43···O11A  0.86  1.89  2.718 (4)  160
N4—H41···O12A  0.90  2.18  3.012 (4)  152
N4—H42···O13A  0.97  2.46  3.369 (4)  155

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

Data collection: CrysAlis PRO (Agilent, 2013); cell refinement: CrysAlis PRO; program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5377).

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4-(4-Aminophenylsulfonyl)anilinium toluene-4-sulfonate

Graham Smith and Urs D. Wermuth

1. Comment

Dapsone [4-(4-aminophenylsulfonyl)aniline] is a very weak Lewis base which finds use as an anti-leprotic, anti-malarial and leprostatic drug (Wilson et al., 1991). The structure of four dapsone solvates are known: the 0.33hydrate (Kus'mina et al., 1981) and the (2:1) dichloromethane, (1:1) 1,4-dioxane and (1:1) tetrahydrofuran solvates (Lemmer et al., 2012) but adducts or salts of this compound are not common. We have reported the structures of a (1:2) co-crystalline adduct with 1,3,5-trinitrobenzene (Smith & Wermuth, 2012a) and (1:1) adds with 3,5-dinitrobenzoic acid (Smith & Wermuth, 2012b) and 5-nitroisophthalic acid (Smith & Wermuth, 2013) but only one proton-transfer salt structure is known, with 3,5-dinitrosalicylic acid (a monohydrate) (Smith & Wermuth, 2013). Reported herein is the structure of a second salt of dapsone, with p-toluenesulfonic acid, C₁₂H₁₃N₂O₂S⁺ C₇H₇O₃S⁻.

In the structure of the title salt (Fig. 1), the conformation of the dapsone monocation as indicated by the inter-ring dihedral angle [70.19 (17)°], compares with 78.27 (9)° in the 3,5-dinitrosalicylic acid salt (Smith & Wermuth, 2013) and 75.4 (2)° in the 3,5-dinitrobenzoic acid adduct (Smith & Wermuth, 2012b). The conformation of the title compound is influenced by short intramolecular ring C—H···Oₐ₆l₂ interactions [C₆—H···O₁₂, 2.918 (4) Å and C₂₁—H···O₁₂, 2.925 (4) Å]. The angles between the p-toluenesulfonate ring and the aniline and anilinium rings respectively, are 46.43 (17)° and 72.34 (17)°.

In the crystal, all amine and aminium H-atoms are involved in intermolecular N—H···O hydrogen-bonding associations with sulfonyl O-atom acceptors as well as with one of the sulfone O-atoms (O11) (Table 1). The resulting structure is a three-dimensional framework (Fig. 2). No π–π interactions are found between the cation and anion ring systems [minimum ring centroid separation = 4.534 (2) Å].

2. Experimental

The title compound was prepared by the reaction of 4-(4-aminophenylsulfonyl)aniline (dapsone) with p-toluenesulfonic acid by heating together for 15 min under reflux, 1 mmol quantities of the two reagents in 50 ml of 50% ethanol–water. Partial room-temperature evaporation of the solvent provided poorly-formed colourless crystal aggregates of the title salt from which a specimen was cleaved for the X-ray analysis.

3. Refinement

All H atoms potentially involved in hydrogen-bonding associations were located in a difference-Fourier analysis but were subsequently constrained, with \( U_{eq}(H) = 1.2 U_{eq}(N) \). Other H-atoms were included at calculated positions [C—H = 0.95 Å (aromatic) or 0.98 Å (methyl)] and also treated as riding, with \( U_{eq}(H) = 1.2 \) or 1.5\( U_{eq}(C) \).

Computing details

Data collection: CrysAlis PRO (Agilent, 2013); cell refinement: CrysAlis PRO (Agilent, 2013); data reduction: CrysAlis PRO (Agilent, 2013); program(s) used to solve structure: SIR92 (Altomare et al., 1993); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).
Figure 1
The molecular conformation and atom-numbering scheme for the dapsone monocation and \( p \)-toluenesulfonate anion in the title salt. Non-H atoms are shown as 40% probability displacement ellipsoids and the inter-species hydrogen bond is shown as a dashed line.
Figure 2
The hydrogen-bonding in the title salt, viewed down the a axial direction of the unit cell. Hydrogen bonds are shown as dashed lines. For symmetry codes see Table 1.

4-(4-Aminophenylsulfonyl)anilinium tolune-4-sulfonate

Crystal data

\[
\begin{align*}
\text{C}_{12}\text{H}_{13}\text{N}_{2}\text{O}_{2}\text{S}^+\cdot\text{C}_7\text{H}_7\text{O}_3\text{S}^- & \quad F(000) = 880 \\
M_r = 420.49 & \quad D_	ext{x} = 1.504 \text{ Mg m}^{-3} \\
\text{Monoclinic, } P2_1/n & \quad \text{Mo K} \delta \text{ radiation, } \lambda = 0.71073 \text{ Å} \\
\text{Hall symbol: } -P 2yn & \quad \text{Cell parameters from 1570 reflections} \\
a = 5.9516 (9) \text{ Å} & \quad \theta = 3.6–27.2^\circ \\
b = 25.147 (3) \text{ Å} & \quad \mu = 0.32 \text{ mm}^{-1} \\
c = 12.4506 (15) \text{ Å} & \quad T = 200 \text{ K} \\
\beta = 94.908 (11)^\circ & \quad \text{Prism, colourless} \\
V = 1856.6 (4) \text{ Å}^3 & \quad 0.25 \times 0.12 \times 0.12 \text{ mm} \\
Z = 4 & \\
\end{align*}
\]

Data collection

\[
\begin{align*}
\text{Oxford Diffraction Gemini-S CCD-detector} & \quad 6908 \text{ measured reflections} \\
\text{Radiation source: Enhance (Mo) X-ray source} & \quad 3650 \text{ independent reflections} \\
\text{Graphite monochromator} & \quad 2653 \text{ reflections with } I > 2\sigma(I) \\
\text{Detector resolution: 16.077 pixels mm}^{-1} & \quad R_{\text{int}} = 0.046 \\
\omega \text{ scans} & \quad \theta_{\text{max}} = 26.0^\circ, \theta_{\text{min}} = 3.2^\circ \\
\text{(CrysAlis PRO; Agilent, 2013)} & \quad h = -7\rightarrow 7 \\
T_{\text{min}} = 0.935, T_{\text{max}} = 0.980 & \quad k = -31\rightarrow 19 \\
& \quad l = -7\rightarrow 15 \\
\end{align*}
\]
supplementary materials

**Refinement**
Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.161$
$S = 1.02$
3650 reflections
253 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 0.6392P]$

$\Delta \rho_{\text{max}} = 0.33 \text{ e Å}^{-3}$
$\Delta \rho_{\text{min}} = -0.39 \text{ e Å}^{-3}$

**Special details**

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**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 (Å²)**

|  | $x$      | $y$      | $z$      | $U_{iso}$/Ueq |
|---|----------|----------|----------|---------------|
|S1| 0.31318 (17)| 0.24657 (3)| 0.40362 (7)| 0.0267 (3)    |
|O11| 0.5538 (5) | 0.25511 (10)| 0.4069 (2)| 0.0372 (9)    |
|O12| 0.1671 (5) | 0.29205 (9)| 0.3968 (2)| 0.0377 (9)    |
|N4| 0.1704 (5) | 0.13828 (12)| 0.8172 (2)| 0.0243 (9)    |
|N41| 0.0383 (6) | 0.10417 (12)| 0.0404 (3)| 0.0344 (10)   |
|C1| 0.2645 (6) | 0.21160 (12)| 0.5225 (3)| 0.0205 (10)   |
|C2| 0.4324 (6) | 0.17907 (14)| 0.5693 (3)| 0.0245 (11)   |
|C3| 0.4005 (6) | 0.15377 (14)| 0.6663 (3)| 0.0247 (11)   |
|C4| 0.2020 (6) | 0.16202 (12)| 0.7128 (3)| 0.0189 (10)   |
|C5| 0.0323 (6) | 0.19321 (13)| 0.6645 (3)| 0.0214 (10)   |
|C6| 0.0637 (6) | 0.21865 (13)| 0.5689 (3)| 0.0230 (11)   |
|C11| 0.2346 (6)| 0.20430 (13)| 0.2959 (3)| 0.0205 (10)   |
|C21| 0.0160 (6)| 0.20665 (14)| 0.2470 (3)| 0.0250 (11)   |
|C31| -0.0465 (6)| 0.17356 (13)| 0.1623 (3)| 0.0241 (11)   |
|C41| 0.1045 (7)| 0.13691 (13)| 0.1250 (3)| 0.0254 (11)   |
|C51| 0.3230 (6)| 0.13441 (14)| 0.1764 (3)| 0.0275 (11)   |
|C61| 0.3863 (6)| 0.16748 (14)| 0.2607 (3)| 0.0261 (12)   |
|S1A| 0.33152 (15)| -0.04463 (3)| 0.14993 (8)| 0.0244 (3)    |
|O11A| 0.1942 (4)| -0.07383 (10)| 0.2210 (2)| 0.0339 (9)    |
|O12A| 0.2028 (4)| -0.00796 (10)| 0.0801 (2)| 0.0331 (9)    |
|O13A| 0.4701 (4)| -0.08006 (10)| 0.0909 (2)| 0.0314 (8)    |
|C1A| 0.5187 (6)| -0.00617 (13)| 0.2370 (3)| 0.0238 (11)   |
|C2A| 0.4538 (6)| 0.00940 (15)| 0.3363 (3)| 0.0306 (12)   |
|C3A| 0.5965 (7)| 0.04085 (15)| 0.4021 (3)| 0.0329 (12)   |
|C4A| 0.8047 (7)| 0.05602 (15)| 0.3713 (3)| 0.0340 (12)   |
|C5A| 0.8647 (6)| 0.04020 (15)| 0.2715 (3)| 0.0315 (12)   |
|C6A| 0.7228 (6)| 0.00919 (14)| 0.2039 (3)| 0.0275 (11)   |

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### Atomic displacement parameters (Å²)

|      |  $U_{11}$   |  $U_{22}$   |  $U_{33}$   |  $U_{12}$   |  $U_{13}$   |  $U_{23}$   |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| S1   | 0.0384 (6)  | 0.0232 (5)  | 0.0178 (5)  | −0.0097 (4) | −0.0024 (4) | 0.0024 (4)  |
| O11  | 0.0397 (17) | 0.0460 (17) | 0.0256 (15) | −0.0258 (14)| 0.0008 (13) | 0.0054 (13) |
| O12  | 0.067 (2)   | 0.0179 (13) | 0.0270 (15) | 0.0014 (13) | −0.0020 (14)| 0.0015 (12) |
| N4   | 0.0212 (16) | 0.0297 (16) | 0.0225 (16) | −0.0006 (13)| 0.0051 (13) | −0.0015 (14) |
| N41  | 0.053 (2)   | 0.0245 (16) | 0.0255 (17) | 0.0009 (15) | 0.0028 (16) | −0.0072 (14) |
| C1   | 0.033 (2)   | 0.0158 (16) | 0.0127 (17) | −0.0093 (15)| 0.0012 (15) | −0.0047 (14) |
| C2   | 0.0224 (19) | 0.032 (2)   | 0.0196 (18) | −0.0037 (16)| 0.0056 (16) | 0.0030 (16)  |
| C3   | 0.0213 (19) | 0.0253 (18) | 0.027 (2)   | 0.0029 (15) | 0.0001 (16) | −0.0011 (16) |
| C4   | 0.0245 (19) | 0.0162 (16) | 0.0162 (17) | −0.0054 (15)| 0.0027 (15) | 0.0006 (14)  |
| C5   | 0.0185 (18) | 0.0260 (18) | 0.0195 (18) | −0.0032 (15)| 0.0010 (15) | −0.0039 (16) |
| C6   | 0.025 (2)   | 0.0253 (18) | 0.0181 (18) | 0.0033 (16) | −0.0014 (16)| −0.0012 (16) |
| C11  | 0.0280 (19) | 0.0205 (17) | 0.0128 (16) | −0.0046 (15)| 0.0015 (15) | 0.0005 (15)  |
| C21  | 0.030 (2)   | 0.0215 (17) | 0.0234 (19) | 0.0017 (16) | 0.0011 (16) | 0.0011 (16)  |
| C31  | 0.026 (2)   | 0.0237 (18) | 0.0213 (18) | −0.0031 (16)| 0.0048 (16) | 0.0011 (16)  |
| C41  | 0.039 (2)   | 0.0172 (17) | 0.0200 (18) | −0.0057 (16)| 0.0033 (17) | 0.0031 (15)  |
| C51  | 0.029 (2)   | 0.0234 (18) | 0.031 (2)   | 0.0055 (16) | 0.0073 (18) | −0.0014 (17) |
| C61  | 0.024 (2)   | 0.029 (2)   | 0.025 (2)   | −0.0019 (16)| 0.0003 (16) | 0.0029 (17)  |
| S1A  | 0.0234 (5)  | 0.0236 (5)  | 0.0251 (5)  | −0.0014 (4) | −0.0042 (4) | 0.0005 (4)   |
| O11A | 0.0294 (15) | 0.0369 (15) | 0.0349 (16) | −0.0134 (12)| −0.0001 (12)| 0.0049 (13)  |
| O12A | 0.0332 (16) | 0.0354 (15) | 0.0290 (15) | 0.0083 (12) | −0.0075 (12)| 0.0059 (13)  |
| O13A | 0.0323 (15) | 0.0293 (13) | 0.0316 (15) | 0.0037 (12) | −0.0027 (12)| −0.0059 (12) |
| C1A  | 0.0204 (19) | 0.0224 (18) | 0.028 (2)   | −0.0016 (15)| −0.0006 (16)| 0.0029 (16)  |
| C2A  | 0.024 (2)   | 0.039 (2)   | 0.029 (2)   | −0.0027 (18)| 0.0030 (17) | 0.0007 (19)  |
| C3A  | 0.038 (2)   | 0.039 (2)   | 0.022 (2)   | −0.0068 (19)| 0.0050 (18) | −0.0029 (18) |
| C4A  | 0.036 (2)   | 0.026 (2)   | 0.038 (2)   | −0.0029 (18)| −0.0075 (19)| −0.0020 (19) |
|    |       |       |       |       |       |       |
|----|-------|-------|-------|-------|-------|-------|
|    | C5A   | 0.025 (2) | 0.033 (2) | 0.037 (2) | −0.0086 (17) | 0.0053 (18) | −0.0017 (19) |
|    | C6A   | 0.030 (2) | 0.0265 (19) | 0.026 (2) | −0.0020 (17) | 0.0023 (17) | −0.0014 (17) |
|    | C41A  | 0.053 (3) | 0.052 (3) | 0.053 (3) | −0.018 (2) | −0.005 (3) | −0.020 (3) |

**Geometric parameters (Å, °)**

| Bond             | Distance (Å) | Angle (°) |
|------------------|--------------|-----------|
| S1—O11           | 1.445 (3)    |           |
| S1—O12           | 1.435 (3)    |           |
| S1—C1            | 1.767 (4)    |           |
| S1—C11           | 1.744 (4)    |           |
| S1A—C1A          | 1.773 (4)    |           |
| S1A—O13A         | 1.455 (3)    |           |
| S1A—O11A         | 1.454 (3)    |           |
| S1A—O12A         | 1.442 (3)    |           |
| N4—C4            | 1.457 (4)    |           |
| N41—C41          | 1.368 (5)    |           |
| N4—H42           | 0.8300       |           |
| N4—H43           | 0.8600       |           |
| N4—H41           | 0.8600       |           |
| N41—H411         | 0.9000       |           |
| N41—H412         | 0.9700       |           |
| C1—C6            | 1.383 (5)    |           |
| C1—C2            | 1.381 (5)    |           |
| C2—C3            | 1.392 (5)    |           |
| C3—C4            | 1.375 (5)    |           |
| C4—C5            | 1.376 (5)    |           |
| C5—C6            | 1.378 (5)    |           |
| C11—C61          | 1.390 (5)    |           |
| C11—C21          | 1.390 (5)    |           |
| C21—C31          | 1.370 (5)    |           |
| C31—C41          | 1.394 (5)    |           |

| Bond             | Distance (Å) | Angle (°) |
|------------------|--------------|-----------|
| O11—S1—O12      | 118.50 (16)  |           |
| O11—S1—C1       | 106.46 (16)  |           |
| O11—S1—C11      | 108.20 (16)  |           |
| O12—S1—C1       | 107.72 (16)  |           |
| O12—S1—C11      | 108.61 (16)  |           |
| C1—S1—C11       | 106.77 (16)  |           |
| O11A—S1A—O13A   | 111.75 (15)  |           |
| O11A—S1A—C1A    | 105.06 (16)  |           |
| O12A—S1A—O13A   | 112.45 (15)  |           |
| O12A—S1A—C1A    | 107.06 (15)  |           |
| O13A—S1A—C1A    | 106.80 (16)  |           |
| O11A—S1A—O12A   | 113.12 (15)  |           |
| C4—N4—H41       | 105.00       |           |
| C4—N4—H42       | 110.00       |           |
| H41—N4—H42      | 111.00       |           |
| H41—N4—H43      | 108.00       |           |
| H42—N4—H43      | 105.00       |           |
| C4—N4—H43       | 118.00       |           |

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| Bond  | Angle          | Bond  | Angle          |
|-------|----------------|-------|----------------|
| C41—N41—H412 | 116.00       | C2A—C1A—C6A | 120.8 (3)       |
| H411—N41—H412  | 120.00       | C1A—C2A—C3A | 119.3 (3)       |
| C41—N41—H411   | 120.00       | C2A—C3A—C4A | 121.0 (3)       |
| S1—C1—C2      | 118.9 (3)    | C3A—C4A—C5A | 118.5 (4)       |
| S1—C1—C6      | 119.7 (3)    | C3A—C4A—C41A| 120.0 (4)       |
| C2—C1—C6      | 121.3 (3)    | C5A—C4A—C41A| 121.5 (4)       |
| C1—C2—C3      | 119.3 (3)    | C4A—C5A—C6A | 121.3 (3)       |
| C2—C3—C4      | 118.8 (3)    | C1A—C6A—C5A | 119.2 (3)       |
| N4—C4—C3      | 119.7 (3)    | C1A—C2A—H2A | 120.00          |
| N4—C4—C5      | 118.5 (3)    | C3A—C2A—H2A | 120.00          |
| C3—C4—C5      | 121.8 (3)    | C2A—C3A—H3A | 120.00          |
| C4—C5—C6      | 119.6 (3)    | C4A—C3A—H3A | 119.00          |
| C1—C6—C5      | 119.2 (3)    | C4A—C5A—H5A | 119.00          |
| S1—C1—C21     | 119.4 (3)    | C6A—C5A—H5A | 119.00          |
| S1—C1—C61     | 120.7 (3)    | C1A—C6A—H6A | 120.00          |
| C21—C11—C61   | 120.0 (3)    | C5A—C6A—H6A | 120.00          |
| C11—C21—C31   | 119.6 (3)    | C4A—C41A—H41A| 109.00         |
| C21—C31—C41   | 121.2 (3)    | C4A—C41A—H42A| 109.00         |
| N41—C41—C51   | 121.3 (3)    | C4A—C41A—H43A| 109.00         |
| N41—C41—C31   | 120.2 (4)    | H41A—C41A—H42A| 110.00        |
| C31—C41—C51   | 118.5 (3)    | H41A—C41A—H43A| 110.00        |
| C41—C51—C61   | 120.5 (3)    | H42A—C41A—H43A| 109.00        |
| C11—C61—C51   | 120.2 (3)    |                   |                |
| O11—S1—C1—C2  | −28.1 (3)    | C2—C3—C4—N4    | −176.6 (3)      |
| O11—S1—C1—C6  | 149.6 (3)    | N4—C4—C5—C6    | 176.2 (3)       |
| O12—S1—C1—C2  | −156.2 (3)   | C3—C4—C5—C6    | −2.5 (5)        |
| O12—S1—C1—C6  | 21.5 (3)     | C4—C5—C6—C1    | 1.0 (5)         |
| C11−S1—C1—C2  | 87.3 (3)     | S1—C11—C61—C51 | 179.8 (3)      |
| C11—S1—C1—C6  | −95.0 (3)    | C61—C11—C21—C31| −1.8 (5)       |
| O11—S1—C11—C2 | −153.5 (3)   | S1—C11—C21—C31 | 180.0 (3)      |
| O11—S1—C11—C6 | 28.2 (3)     | C21—C11—C61—C51| 1.6 (5)        |
| O12—S1—C11—C2 | −23.7 (3)    | C11—C21—C31—C41| 0.9 (5)       |
| O12—S1—C11—C6 | 158.1 (3)    | C21—C31—C41—N41| 179.9 (3)     |
| C1—S1—C11—C21 | 92.2 (3)     | C21—C31—C41—C51| 0.2 (5)       |
| C1—S1—C11—C61 | −86.0 (3)    | C31—C41—C51—C61| −0.4 (5)      |
| O12A−S1A—C1A—C2A| 92.7 (3)    | N41—C41—C51—C61| 179.9 (3)     |
| O12A−S1A—C1A—C6A| −85.3 (3)   | C41—C51—C61—C11| −0.5 (5)      |
| O13A−S1A—C1A—C2A| −146.7 (3) | S1A—C1A—C2A—C3A| −177.7 (3)    |
| O13A−S1A—C1A—C6A| 35.4 (3)    | C6A—C1A—C2A—C3A| 0.2 (5)       |
| O11A−S1A—C1A—C2A| −27.8 (3)   | S1A—C1A—C6A—C5A| 178.5 (3)     |
| O11A−S1A—C1A—C6A| 154.2 (3)   | C2A—C1A—C6A—C5A| 0.5 (5)       |
| S1—C1—C2—C3   | 176.3 (3)    | C1A—C2A—C3A—C4A| −1.4 (6)      |
| C2—C1—C6—C5   | 0.9 (5)      | C2A—C3A—C4A—C5A| 1.8 (6)       |
| C6—C1—C2—C3   | −1.4 (5)     | C2A—C3A—C4A—C41A| −177.9 (4)   |
| S1—C1—C6—C5   | −176.8 (3)   | C3A—C4A—C5A—C6A| −1.0 (6)      |
| C1—C2—C3—C4   | −0.1 (5)     | C41A—C4A—C5A—C6A| 178.7 (4)    |
| C2—C3—C4—C5   | 2.0 (5)      | C4A—C5A—C6A—C1A| −0.1 (6)      |
### Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A   | D—H···A |
|---------|------|-------|---------|---------|
| N4—H41···O13Ai | 0.86 | 1.91  | 2.759 (4) | 165     |
| N4—H42···O11i | 0.83 | 2.24  | 3.008 (4) | 153     |
| N4—H43···O11.4iii | 0.86 | 1.89  | 2.718 (4) | 160     |
| N41—H411···O12A | 0.90 | 2.18  | 3.012 (4) | 152     |
| N41—H412···O13.4iv | 0.97 | 2.46  | 3.369 (4) | 155     |
| C2—H2···O11 | 0.95 | 2.59  | 2.918 (4) | 101     |
| C2A—H2A···O11A | 0.95 | 2.56  | 2.907 (4) | 102     |
| C6—H6···O12 | 0.95 | 2.59  | 2.933 (4) | 102     |
| C21—H21···O12 | 0.95 | 2.58  | 2.935 (4) | 102     |

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