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Smith, Graham & Wermuth, Urs D. (2014) Crystal structures and hydrogen bonding in the proton transfer salts of nicotine with 3,5-dinitrosalicylic acid and 5-sulfosalicylic acid. *Acta Crystallographica. Section E: Structure Reports Online*, 70, pp. 430-434.

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https://doi.org/10.1107/S1600536814023253
Crystal structures and hydrogen bonding in the proton-transfer salts of nicotine with 3,5-dinitrosalicylic acid and 5-sulfosalicylic acid

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Acta Cryst. (2014). E70, 430–434
Crystal structures and hydrogen bonding in the proton-transfer salts of nicotine with 3,5-dinitrosalicylic acid and 5-sulfosalicylic acid

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The structures of the 1:1 anhydrous salts of nicotine (NIC) with 3,5-dinitrosalicylic acid (DNSA) and 5-sulfosalicylic acid (5-SSA), namely (1R,2S)-1-methyl-2-(pyridin-3-yl)-1H-pyrrolidin-1-ium 2-carboxy-4,6-dinitrophenolate, C_{10}H_{15}N_{2}+C_{7}H_{3}N_{2}O_{7}−, (I), and (1R,2S)-1-methyl-2-(pyridin-3-yl)-1H-pyrrolidin-1-ium 3-carboxy-4-hydroxybenzenesulfonate, C_{10}H_{15}N_{2}+C_{7}H_{5}O_{6}S−, (II), are reported. The asymmetric units of both (I) and (II) comprise two independent nicotinium cations (C and D) and either two DNSA or two 5-SSA anions (A and B), respectively. One of the DNSA anions shows a 25% rotational disorder in the benzene ring system. In the crystal of (I), inter-unit pyrrolidinium N—H/C1/C1/C1Npyridine hydrogen bonds generate zigzag NIC cation chains which extend along a, while the DNSA anions are not involved in any formal inter-species hydrogen bonding but instead form π–π-associated stacks which are parallel to the NIC cation chains along a [ring-centroid separation = 3.857 (2) Å]. Weak C—H/C1/C1/C1O interactions between chain substructures give an overall three-dimensional structure. In the crystal of (II), A and B anions form independent zigzag chains with C and D cations, respectively, through carboxylic acid O—H···Npyridine hydrogen bonds. These chains, which extend along b, are pseudocentrosymmetrically related and give π–π interactions between the benzene rings of anions A and B and the pyridine rings of the NIC cations C and D, respectively [ring centroid separations = 3.6422 (19) and 3.7117 (19) Å]. Also present are weak C—H···O hydrogen-bonding interactions between the chains, giving an overall three-dimensional structure.

1. Chemical context

Nicotine [3-(2S-1-methylpyrrolidin-2-yl)pyridine] is well known as a toxic liquid alkaloid which is found in the leaves of the tobacco plants Nicotiana tabacum and N. rustica (Rodgman & Parfetti, 2009). Because of these properties, nicotine and its compounds have been of commercial interest and have been used in the past as insecticides and as veterinary ectoparasiticides (usually as the sulfate) (Ujváry, 1999), as well as in limited medical applications as the bitartrate (Eudermol) for the treatment of smoking-withdrawal syndrome (Enzell et al., 1977). However, its veterinary use is restricted due to its toxicity with even topical applications, resulting in the total ban on its use in the USA early in 2014.

As a Lewis base, nicotine is potentially capable of forming both monocationic and dicationic species (pK_{a1} = 3.10 and pK_{a2} = 8.01) and the sulfate, dihydrochloride, bitartrate and bipicrate salts have been reported (O’Neil, 2001). However, the only example of a simple dicationic salt in the crystallographic literature is the dihydroiodide (Koo & Kim, 1965). Some metal complexes with the dication as a counter-ion are known, e.g. tetrachloridocopper(II) nicotinate (Choi et al.,...
5-SSA) (pK_a = 2.18) and 3-carboxyl-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid: 5-SSA) (pK_a < 1) are capable of forming salts with most Lewis bases and have been used for the formation of crystalline salts suitable for X-ray analysis, e.g. with 5-SSA (Baskar Raj et al., 2003; Smith et al., 2006) and with DNSA, where the majority of the salts formed are phenolates rather than carboxylates (Smith et al., 2007). The title salts C_{10}H_{15}N_2^+ C_7H_5O_6S^- (I) and C_{10}H_{15}N_2^+ C_7H_3O_7^- (II) were prepared from the reaction of nicotine (NIC) with DNSA and with 5-SSA, respectively, and the structures are reported herein.

2. Structural commentary

In both the nicotinium salts of DNSA (I) and 5-SSA (II), proton-transfer to the pyrrolidine N-atom of nicotine has occurred as expected, generating an N11(R) chiral centre relative to the known C21(S) centre. Also, in both (I) and (II) (Figs. 1 and 2), the asymmetric units comprise two independent NIC cations (C and D) and either, for (I), two DNSA phenolate monoanions or two 5-SSA carboxylate monoanions (A and B) (Figs. 1, 2). With (II), the two independent anion and cation pairs are pseudo-centrosymmetrically related but the presence of the inversion centre is obviated by the fact that both of the NIC cations have the same N11(R), C21(S) absolute configuration.

In (I), the nicotinium C and D cations are conformationally similar but in (II), they are different. However, in both, the pyrrolidinium plane is significantly rotated with respect to that of the benzene ring [the torsion angles C2/C/D/C3/C/D — C21/C/D — N11/C/D are —71.9 (4) (C) and —68.8 (4°) (D) in (I) and —45.7 (4) (C) and 125.7 (3°) (D) in (II)]. This conformation with the two rings anti-planar is usual for cationic nicotine structures, e.g. Arnaud et al. (2007). The substituent carboxyl and nitro groups of the DNSA anions in (I) are essentially coplanar with the benzene ring, with the maximum deviation among the three defining torsion angles for each anion (C2A/B — C1A/B — C11A/B — O2A/B, C2A/B — C3A/B — N3A/B — O32A/B and C4A/B — C5A/B — N5A/B — O52A/B) being for the C3B nitro group [173.7 (3°)]. In the B anion, there is 25% rotational disorder about the C1 · · · C4 ring vector, which generates a second phenolic O-component (O21B). This phenomenon has precedence in DNSA salt structures, e.g. with the nicotinamide salt (Koman et al., 2003; 24% disorder). The C3 nitro group is most often associated with deviation from planarity in the DNSA phenolate salts (Smith et al., 2007) and is the more interactive and sterically crowded group. In the case of (I), the uncommon planarity is probably associated with the presence of anion σ-bonding associations.

With the 5-SSA anions, the carboxylic acid group is essentially coplanar with the benzene ring, which is expected in this salicylic acid species, invariably having the short intramolecular carboxylic acid O—H · · · Ophenol hydrogen bond (Table 2) (Smith et al., 2006). This interaction is also present in the phenolate anion in (I) in which the carboxylic acid H-atom is anti-related (Table 1).

Figure 1

The molecular conformation and atom labelling for the two NIC cations (C and D) and the two DNSA anions (A and B) in the asymmetric unit of (I), with displacement ellipsoids drawn at the 40% probability level. Inter-species hydrogen bonds are shown as dashed lines (see Table 1).

Figure 2

The molecular conformation and atom labelling for the two NIC cations (C and D) and the two 5-SSA anions (A and B) in the asymmetric unit of (II), with displacement ellipsoids drawn at the 40% probability level. Inter-species hydrogen bonds are shown as dashed lines (see Table 2).
3. Supramolecular features

In the supramolecular structure of (I), the two independent NIC cations C and D interact through NIC – H···N11D' and N11D – H···N1IC hydrogen bonds (Table 1), giving zigzag chains extending along a (Fig. 3). With the DNSA anions, there are no formal hydrogen-bonding interactions either between A and B anions or with the NIC chain structures. Instead, these anions form π–π interactions (i) and with anion stacks in the structure of (I), viewed along the stacks in the unit cell.

The alternating hydrogen-bonded C–D cationic columns and π-bonded A–B anion stacks which are bonded links between the two chains, there are π–π interactions between 5-SSA anion A and B benzene rings and C and D NIC cation pyridine rings, respectively [ring-centroid separations = 3.6422 (19) and 3.7117 (19) Å] (Fig. 4). The presence of a number of intermolecular C–H···O hydrogen-bonding interactions to carboxyl, nitro and phenolic O-atom acceptors gives rise to an overall three-dimensional structure.

| Table 1 Hydrogen-bond geometry (Å, °) for (I). |
|-----------------------------------------------|
| \( D - H \cdot \cdot \cdot A \) | \( D - H \) | \( H \cdot \cdot \cdot A \) | D – A | \( D - H \cdot \cdot \cdot A \) |
| O12A – H12A – O2A | 0.84 | 1.71 | 2.475 (4) | 150 |
| O12B – H12B – O2B | 0.84 | 1.63 | 2.411 (4) | 152 |
| N11C – H11C – N1D' | 0.93 | 1.89 | 2.809 (4) | 169 |
| N11D – H11D – N1IC | 0.93 | 1.90 | 2.817 (5) | 168 |
| C2C – H2C – O11A’ | 0.95 | 2.42 | 3.228 (5) | 143 |
| C4C – H4C – O31A’ | 0.95 | 2.59 | 3.452 (5) | 151 |
| C6C – H6C – O32A” | 0.95 | 2.27 | 3.054 (5) | 139 |
| C11C – H13C – O32B’ | 0.98 | 2.48 | 3.151 (6) | 126 |
| C11D – H14D – O51A” | 0.98 | 2.55 | 3.373 (6) | 141 |
| C21C – H21C – O2A’ | 1.00 | 2.27 | 3.163 (5) | 148 |
| C21D – H21D – O11B’ | 1.00 | 2.44 | 3.307 (5) | 144 |
| C51C – H52C – O11A” | 0.99 | 2.54 | 3.534 (6) | 177 |

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

| Table 2 Hydrogen-bond geometry (Å, °) for (II). |
|-----------------------------------------------|
| \( D - H \cdot \cdot \cdot A \) | \( D - H \) | \( H \cdot \cdot \cdot A \) | D – A | \( D - H \cdot \cdot \cdot A \) |
| O2A – H2A – O12A | 0.84 | 1.80 | 2.549 (4) | 147 |
| O2B – H2B – O12B | 0.84 | 1.82 | 2.501 (4) | 146 |
| O11A – H11A – N1D | 0.95 | 1.60 | 2.555 (4) | 179 |
| O11B – H11B – N1C | 0.95 | 1.61 | 2.558 (4) | 179 |
| N11C – H11C – O51B’ | 0.93 | 2.32 | 3.022 (5) | 132 |
| N11C – H11C – O53B’ | 0.93 | 2.15 | 3.029 (5) | 157 |
| N11D – H11D – O52A” | 0.93 | 1.85 | 2.735 (5) | 189 |
| C2C – H2C – O53B’ | 0.95 | 2.29 | 3.201 (5) | 160 |
| C2C – H2C – O52A” | 0.95 | 2.45 | 3.359 (4) | 160 |
| C11C – H12C – O2A’ | 0.98 | 2.52 | 3.481 (5) | 165 |
| C11C – H13C – O52B” | 0.98 | 2.46 | 3.290 (5) | 142 |
| C11D – H14D – O51A” | 0.98 | 2.37 | 3.251 (5) | 150 |
| C21C – H21C – O52B” | 1.00 | 2.42 | 3.331 (5) | 151 |

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

Figure 3
The alternating hydrogen-bonded C–D cationic columns and π-bonded A–B anion stacks which are parallel to the NIC chains down a [ring-centroid separation = 3.857 (2) Å]. The presence of π–π stacking is unusual in DNSA cation structures. In the crystal, there is a number of intermolecular CC/D – H···O/A/B hydrogen-bonding interactions, which give an overall three-dimensional structure.

In the crystal of (II), the independent A and B 5-SSA anions form carboxylic acid O–H···Npyridine hydrogen bonds with the D and C NIC cations, respectively (Table 2) (see Fig. 2). These cation–anion subunits are then extended into independent chain structures through pyrrolidinium N–H···OSulfonate hydrogen bonds, which with anion C is three-centre (O51B’ and O53B’) and with anion D, linear (O52A”). These give independent zigzag chain substructures which extend along b. Although there are no formal hydrogen-
4. Synthesis and crystallization

The title salts (I) and (II) were prepared by refluxing equimolar quantities of nicotine (160 mg) and the respective acids, 3,5-dinitrosalicylic acid (230 mg) for (I) or 3-carboxy-4-hydroxybenzenesulfonic acid (220 mg) for (II) in 30 ml of ethanol for 10 min, after which room temperature evaporation of the solutions gave, for (I), thin yellow needles and for (II) colourless prisms, from which specimens were cleaved for the X-ray analyses.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms on all potentially intermolecular O—H and N—H groups in all molecular species, were located by difference-Fourier methods but these and the carbon-bound H-atoms were subsequently set as riding on the parent atoms in the refinement in calculated positions [O—H = 0.88, N—H = 0.94, C—H = 0.95–1.00 Å] and with $U_{	ext{iso}}$(H) = 1.5$U_{	ext{eq}}$(O or methyl-C) or 1.2$U_{	ext{eq}}$(C, N).

In both structures, the known C21(S) absolute configuration was invoked. The Flack parameter for (I) [0.2 (16)] has no physical meaning. The absolute structure of compound (II) was confirmed by resonant scattering [Flack parameter = −0.02 (9)].

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Crystal structures and hydrogen bonding in the proton-transfer salts of nicotine with 3,5-dinitrosalicylic acid and 5-sulfosalicylic acid

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Computing details
For both compounds, data collection: CrysAlis PRO (Agilent, 2013); cell refinement: CrysAlis PRO (Agilent, 2013); data reduction: CrysAlis PRO (Agilent, 2013). Program(s) used to solve structure: SHELXS97 (Sheldrick, 2008) for (I); SIR92 (Altomare et al., 1993) for (II). For both compounds, 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 (Spek, 2009).

(I) (1R,2S)-1-Methyl-2-(pyridin-3-yl)pyrrolidin-1-ium 2-carboxy-4,6-dinitrophenolate

Crystal data

C_{10}H_{15}N_{2}^{+}\cdotC_{7}H_{3}N_{2}O_{7}^{-}

F(000) = 1632

D_{x} = 1.470 Mg m^{-3}

Mo Kα radiation, λ = 0.71073 Å

Cell parameters from 1206 reflections

θ = 3.6–22.4°

µ = 0.12 mm^{-1}

T = 200 K

Needle, yellow

0.40 × 0.10 × 0.08 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, 2013)

T_{min} = 0.807, T_{max} = 0.980

Refinement

Refinement on F^{2}

Least-squares matrix: full

R[F^{2} > 2σ(F^{2})] = 0.072

wR(F^{2}) = 0.122

S = 1.07

6476 reflections

508 parameters

2 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
supporting information

\[ w = \frac{1}{(\sigma^2 F^2_P + 0.0329 P^2)^2} \]

\[ \text{where } P = \frac{(F^2_o + 2F^2_c)}{3} \]

\[ \Delta \sigma_{\text{max}} = 0.001 \]

\[ \Delta \rho_{\text{max}} = 0.44 \text{ e Å}^{-3} \]

**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 (Å\(^2\))**

| x   | y       | z       | \( U_{eq} \) | Occ. (<1) |
|-----|---------|---------|--------------|-----------|
| O2B | 0.7440 (5) | -0.0370 (2) | 0.16873 (13) | 0.0543 (14) | 0.750 |
| O11B | 0.7783 (6) | -0.17264 (18) | 0.06034 (13) | 0.0812 (15) |
| O12B | 0.7503 (5) | -0.16123 (18) | 0.13451 (12) | 0.0722 (15) |
| O31B | 0.7213 (6) | 0.1013 (2) | 0.19951 (11) | 0.0867 (16) |
| O32B | 0.8016 (5) | 0.19443 (18) | 0.15674 (11) | 0.0645 (14) |
| O51B | 0.9215 (5) | 0.16351 (18) | 0.00036 (11) | 0.0653 (14) |
| O52B | 0.9011 (5) | 0.05377 (19) | -0.03182 (10) | 0.0614 (11) |
| N3B | 0.7691 (5) | 0.1272 (2) | 0.16280 (13) | 0.0440 (14) |
| N5B | 0.8927 (5) | 0.0950 (2) | 0.00167 (12) | 0.0433 (12) |
| C1B | 0.7883 (5) | -0.0493 (2) | 0.09179 (14) | 0.0327 (14) |
| C2B | 0.7715 (5) | -0.0035 (2) | 0.13069 (13) | 0.0337 (14) |
| C3B | 0.7884 (5) | 0.0757 (2) | 0.12439 (13) | 0.0283 (12) |
| C4B | 0.8272 (5) | 0.1069 (2) | 0.08283 (13) | 0.0300 (11) |
| C5B | 0.8439 (5) | 0.0611 (2) | 0.04550 (13) | 0.0287 (12) |
| C6B | 0.8230 (5) | -0.0181 (2) | 0.04906 (14) | 0.0333 (12) |
| C11B | 0.7727 (7) | -0.1329 (3) | 0.09462 (19) | 0.0543 (19) |
| O21B | 0.8109 (16) | -0.0648 (7) | 0.0169 (4) | 0.0543 (14) | 0.250 |
| O2A | 0.2427 (6) | 0.14566 (18) | 0.18109 (11) | 0.0750 (14) |
| O11A | 0.1135 (5) | 0.0131 (2) | 0.28861 (10) | 0.0655 (14) |
| O12A | 0.1240 (5) | 0.1263 (2) | 0.25992 (10) | 0.0650 (12) |
| O31A | 0.3353 (5) | 0.1552 (2) | 0.09522 (11) | 0.0723 (16) |
| O32A | 0.3389 (5) | 0.0535 (2) | 0.05553 (11) | 0.0784 (15) |
| O51A | 0.2682 (6) | -0.18960 (19) | 0.11877 (14) | 0.0817 (16) |
| O52A | 0.2223 (6) | -0.20342 (18) | 0.19127 (14) | 0.0889 (15) |
| N3A | 0.3211 (5) | 0.0872 (2) | 0.09182 (13) | 0.0470 (14) |
| N5A | 0.2457 (6) | -0.1639 (2) | 0.15757 (18) | 0.0603 (16) |
| C1A | 0.2002 (5) | 0.0247 (2) | 0.21164 (13) | 0.0333 (12) |
| C2A | 0.2429 (5) | 0.0748 (2) | 0.17458 (14) | 0.0333 (14) |
| C3A | 0.2821 (5) | 0.0401 (2) | 0.13212 (13) | 0.0287 (12) |
| C4A | 0.2834 (5) | -0.0373 (2) | 0.12566 (14) | 0.0350 (16) |
| C5A | 0.2445 (5) | -0.0816 (2) | 0.16347 (16) | 0.0383 (14) |
| C6A | 0.2026 (5) | -0.0513 (2) | 0.20552 (14) | 0.0370 (16) |

**Absolute structure:** Flack (1983), 2983 Friedel pairs

**Absolute structure parameter:** −0.2 (16)
C11A 0.1438 (6) 0.0551 (3) 0.25629 (15) 0.0397 (16)  
N1C 0.9322 (4) 0.46384 (19) 0.08412 (11) 0.0342 (11)  
N11C 1.3932 (4) 0.34882 (17) 0.16230 (10) 0.0325 (10)  
C2C 1.0225 (5) 0.4293 (2) 0.11887 (13) 0.0297 (12)  
C3C 1.0826 (5) 0.3546 (2) 0.11738 (12) 0.0267 (12)  
C4C 1.0488 (5) 0.3140 (2) 0.07781 (13) 0.0367 (12)  
C5C 0.9526 (6) 0.3489 (3) 0.04199 (14) 0.0400 (16)  
C6C 0.8990 (6) 0.4232 (3) 0.04661 (14) 0.0413 (16) 
C11C 1.5274 (6) 0.3279 (3) 0.12449 (13) 0.0437 (17)  
C21C 1.1861 (5) 0.3191 (2) 0.15719 (12) 0.0297 (12)  
C31C 1.4563 (6) 0.3212 (3) 0.20791 (14) 0.0483 (17)  
C41C 1.2739 (7) 0.3266 (3) 0.23712 (14) 0.0563 (18)  
C51C 1.0999 (6) 0.3309 (3) 0.20426 (12) 0.0447 (16)  
N1D 0.4269 (4) 0.50744 (17) 0.16513 (11) 0.0331 (10)  
N11D 0.8855 (4) 0.62248 (19) 0.08623 (11) 0.0349 (11)  
C2D 0.5212 (5) 0.5403 (2) 0.13071 (14) 0.0330 (12)  
C3D 0.5708 (5) 0.6165 (2) 0.12973 (13) 0.0300 (12)  
C4D 0.5191 (5) 0.6592 (2) 0.16646 (14) 0.0373 (14)  
C5D 0.4196 (6) 0.6276 (2) 0.20240 (14) 0.0423 (17)  
C6D 0.3794 (6) 0.5509 (2) 0.20076 (14) 0.0393 (14)  
C11D 1.0141 (6) 0.6465 (3) 0.12373 (14) 0.0507 (16)  
C21D 0.6765 (5) 0.6508 (2) 0.08995 (12) 0.0330 (12)  
C31D 0.5957 (6) 0.6372 (3) 0.04297 (14) 0.0560 (17)  
C41D 0.7691 (8) 0.6443 (3) 0.01105 (15) 0.075 (2)   
C51D 0.9507 (7) 0.6480 (3) 0.03995 (14) 0.0557 (17)  
H6B 0.83210 −0.04960 0.02280 0.0400* 0.750     
H12B 0.73670 −0.12610 0.15360 0.1080* 0.750     
H4B 0.84250 0.16020 0.07990 0.0360*           
H2B 0.74970 −0.02470 0.16000 0.0410* 0.250     
H11B 0.79170 −0.14500 0.03730 0.1220* 0.250     
H4A 0.30970 −0.05920 0.09670 0.0420*           
H6A 0.17520 −0.08390 0.23050 0.0450*           
H12A 0.17450 0.14760 0.23720 0.0970*           
H2C 1.04650 0.45760 0.14580 0.0360*           
H4C 1.09110 0.26290 0.07530 0.0440*           
H5C 0.92430 0.32190 0.01480 0.0480*           
H6C 0.83470 0.44720 0.02180 0.0500*           
H11C 1.38680 0.40140 0.16350 0.0390*           
H12C 1.47550 0.34780 0.09570 0.0660*           
H13C 1.53770 0.27260 0.12260 0.0660*           
H14C 1.65760 0.34960 0.13010 0.0660*           
H21C 1.19410 0.26330 0.15160 0.0350*           
H31C 1.56270 0.35340 0.22040 0.0580*           
H32C 1.50340 0.26820 0.20610 0.0580*           
H41C 1.27900 0.37250 0.25650 0.0680*           
H42C 1.26220 0.28150 0.25700 0.0680*           
H51C 1.00240 0.29100 0.21130 0.0530*           
H52C 1.03470 0.38100 0.20630 0.0530*           
H2D 0.55660 0.50980 0.10530 0.0400*
H4D 0.55240 0.71140 0.16720 0.0450*
H5D 0.37950 0.65750 0.22760 0.0510*
H6D 0.31540 0.52800 0.22600 0.0470*
H11D 1.14600 0.62570 0.11900 0.0760*
H13D 0.96120 0.62770 0.15270 0.0760*
H14D 1.02080 0.70200 0.12450 0.0760*
H21D 0.68180 0.70690 0.09490 0.0400*
H31D 0.49390 0.67530 0.03550 0.0670*
H32D 0.53690 0.58600 0.04080 0.0670*
H41D 0.77510 0.60010 −0.00960 0.0900*
H42D 0.75700 0.69090 −0.00760 0.0900*
H51D 1.05380 0.61390 0.02780 0.0670*
H52D 1.00290 0.70030 0.04110 0.0670*

Atomic displacement parameters (Å²)

|   | U¹¹   | U¹²   | U¹³   | U²²   | U²³   | U³³   |
|---|-------|-------|-------|-------|-------|-------|
| O2B | 0.059 (2) | 0.060 (3) | 0.044 (2) | 0.001 (2) | 0.001 (2) | 0.008 (2) |
| O11B | 0.126 (3) | 0.0287 (19) | 0.089 (3) | −0.005 (2) | 0.007 (3) | −0.007 (2) |
| O12B | 0.093 (3) | 0.0386 (19) | 0.085 (3) | −0.010 (2) | −0.006 (2) | 0.021 (2) |
| O31B | 0.134 (3) | 0.082 (3) | 0.044 (2) | −0.006 (3) | 0.031 (2) | −0.015 (2) |
| O32B | 0.092 (3) | 0.0375 (19) | 0.064 (2) | 0.0084 (19) | −0.008 (2) | −0.0172 (19) |
| O51B | 0.101 (3) | 0.039 (2) | 0.056 (2) | −0.018 (2) | 0.0012 (19) | 0.0146 (18) |
| O52B | 0.095 (2) | 0.060 (2) | 0.0291 (17) | 0.011 (2) | 0.0128 (17) | 0.0013 (17) |
| N3B | 0.040 (2) | 0.053 (3) | 0.039 (2) | 0.003 (2) | −0.0037 (18) | −0.009 (2) |
| N5B | 0.046 (2) | 0.047 (2) | 0.037 (2) | 0.001 (2) | 0.0006 (18) | 0.008 (2) |
| C1B | 0.030 (2) | 0.028 (2) | 0.040 (3) | 0.0029 (19) | −0.0067 (19) | 0.005 (2) |
| C2B | 0.024 (2) | 0.048 (3) | 0.029 (2) | 0.002 (2) | 0.0015 (18) | 0.013 (2) |
| C3B | 0.023 (2) | 0.033 (2) | 0.029 (2) | 0.0040 (18) | 0.0008 (18) | −0.005 (2) |
| C4B | 0.0269 (19) | 0.026 (2) | 0.037 (2) | 0.0032 (18) | −0.0050 (19) | 0.000 (2) |
| C5B | 0.032 (2) | 0.029 (2) | 0.025 (2) | 0.0009 (18) | 0.0003 (17) | 0.0052 (19) |
| C6B | 0.035 (2) | 0.027 (2) | 0.038 (2) | 0.0014 (19) | 0.001 (2) | −0.008 (2) |
| C11B | 0.056 (3) | 0.031 (3) | 0.076 (4) | −0.004 (3) | −0.008 (3) | 0.013 (3) |
| O21B | 0.059 (2) | 0.060 (3) | 0.044 (2) | 0.001 (2) | 0.002 (2) | 0.008 (2) |
| O2A | 0.110 (3) | 0.0401 (19) | 0.075 (2) | 0.004 (2) | −0.011 (2) | 0.006 (2) |
| O11A | 0.081 (2) | 0.078 (3) | 0.0375 (19) | −0.013 (2) | 0.0043 (18) | 0.002 (2) |
| O12A | 0.085 (2) | 0.059 (2) | 0.051 (2) | 0.004 (2) | 0.0026 (17) | −0.012 (2) |
| O31A | 0.104 (3) | 0.040 (2) | 0.073 (3) | 0.011 (2) | 0.027 (2) | 0.026 (2) |
| O32A | 0.110 (3) | 0.095 (3) | 0.0302 (18) | −0.012 (3) | 0.008 (2) | 0.006 (2) |
| O51A | 0.097 (3) | 0.044 (2) | 0.104 (3) | −0.001 (2) | 0.008 (3) | −0.031 (2) |
| O52A | 0.117 (3) | 0.0316 (19) | 0.118 (3) | 0.004 (2) | 0.024 (3) | 0.019 (2) |
| N3A | 0.035 (2) | 0.062 (3) | 0.044 (2) | 0.006 (2) | 0.0001 (18) | 0.014 (2) |
| N5A | 0.057 (3) | 0.034 (2) | 0.090 (3) | −0.002 (2) | 0.006 (3) | −0.003 (3) |
| C1A | 0.032 (2) | 0.035 (2) | 0.033 (2) | 0.000 (2) | −0.0052 (19) | 0.004 (2) |
| C2A | 0.028 (2) | 0.023 (2) | 0.049 (3) | 0.005 (2) | −0.010 (2) | 0.005 (2) |
| C3A | 0.028 (2) | 0.033 (2) | 0.025 (2) | 0.0035 (19) | 0.0006 (18) | 0.011 (2) |
|    |     |     |     |     |     |     |
|----|-----|-----|-----|-----|-----|-----|
| C4A | 0.023 (2) | 0.043 (3) | 0.039 (3) | 0.005 (2) | −0.0039 (19) | 0.002 (2) |
| C5A | 0.031 (2) | 0.025 (2) | 0.059 (3) | 0.001 (2) | −0.002 (2) | 0.003 (2) |
| C6A | 0.032 (2) | 0.039 (3) | 0.040 (3) | 0.003 (2) | 0.003 (2) | 0.015 (2) |
| C11A | 0.037 (2) | 0.042 (3) | 0.040 (3) | −0.004 (2) | −0.004 (2) | −0.003 (2) |
| N1C | 0.0364 (18) | 0.036 (2) | 0.0303 (19) | 0.00067 (16) | −0.00343 (17) | 0.0030 (16) |
| C2C | 0.036 (2) | 0.030 (2) | 0.023 (2) | 0.0014 (19) | 0.0002 (17) | 0.001 (2) |
| C3C | 0.028 (2) | 0.020 (2) | 0.032 (2) | −0.0048 (18) | 0.0048 (17) | 0.0000 (19) |
| C4C | 0.042 (2) | 0.029 (2) | 0.039 (2) | −0.003 (2) | 0.007 (2) | −0.006 (2) |
| C5C | 0.050 (3) | 0.041 (3) | 0.029 (2) | 0.000 (2) | −0.007 (2) | −0.003 (2) |
| C6C | 0.045 (3) | 0.045 (3) | 0.034 (2) | 0.008 (2) | −0.004 (2) | 0.005 (2) |
| C11C | 0.041 (3) | 0.046 (3) | 0.044 (3) | 0.009 (2) | 0.006 (2) | 0.003 (2) |
| C21C | 0.036 (2) | 0.019 (2) | 0.034 (2) | −0.0047 (17) | 0.0022 (19) | 0.0007 (19) |
| C31C | 0.060 (3) | 0.044 (3) | 0.041 (3) | 0.005 (2) | −0.017 (2) | 0.010 (2) |
| C41C | 0.087 (4) | 0.053 (3) | 0.029 (2) | −0.006 (3) | −0.004 (3) | 0.003 (2) |
| C51C | 0.061 (3) | 0.042 (3) | 0.031 (2) | 0.007 (2) | 0.008 (2) | 0.009 (2) |
| N1D | 0.0535 (17) | 0.0241 (17) | 0.040 (2) | −0.0021 (16) | −0.0002 (17) | 0.0004 (18) |
| N11D | 0.0427 (19) | 0.0271 (18) | 0.0349 (19) | −0.0011 (17) | 0.0062 (16) | 0.0028 (17) |
| C2D | 0.033 (2) | 0.029 (2) | 0.037 (2) | 0.003 (2) | 0.0023 (19) | −0.003 (2) |
| C3D | 0.029 (2) | 0.026 (2) | 0.035 (2) | 0.0002 (19) | −0.0037 (19) | 0.002 (2) |
| C4D | 0.041 (2) | 0.022 (2) | 0.049 (3) | −0.0043 (19) | 0.001 (2) | −0.005 (2) |
| C5D | 0.049 (3) | 0.038 (3) | 0.040 (3) | 0.000 (2) | 0.009 (2) | −0.009 (2) |
| C6D | 0.042 (2) | 0.035 (2) | 0.041 (3) | −0.004 (2) | 0.008 (2) | −0.001 (2) |
| C11D | 0.039 (2) | 0.056 (3) | 0.057 (3) | −0.008 (2) | −0.008 (2) | 0.002 (3) |
| C21D | 0.035 (2) | 0.025 (2) | 0.039 (2) | 0.0035 (19) | 0.0007 (19) | 0.001 (2) |
| C31D | 0.063 (3) | 0.060 (3) | 0.045 (3) | −0.012 (3) | −0.016 (3) | 0.019 (3) |
| C41D | 0.113 (4) | 0.074 (4) | 0.038 (3) | 0.010 (4) | 0.001 (3) | 0.000 (3) |
| C51D | 0.071 (3) | 0.045 (3) | 0.051 (3) | 0.008 (3) | 0.031 (3) | 0.013 (3) |

**Geometric parameters (Å, °)**

|    |     |     |     |     |     |     |
|----|-----|-----|-----|-----|-----|-----|
| O2B—C2B | 1.277 (5) | C4A—C5A | 1.383 (6) |
| O11B—C11B | 1.227 (7) | C5A—C6A | 1.375 (6) |
| O12B—C11B | 1.283 (7) | C4A—H4A | 0.9500 |
| O21B—C6B | 1.256 (13) | C6A—H6A | 0.9500 |
| O31B—N3B | 1.215 (5) | C2C—C3C | 1.381 (5) |
| O32B—N3B | 1.222 (5) | C3C—C21C | 1.502 (5) |
| O51B—N5B | 1.225 (5) | C3C—C4C | 1.384 (5) |
| O52B—N5B | 1.224 (5) | C4C—C5C | 1.384 (6) |
| O11B—H11B | 0.8400 | C5C—C6C | 1.367 (7) |
| O12B—H12B | 0.8400 | C21C—C51C | 1.516 (5) |
| O2A—C2A | 1.265 (5) | C31C—C41C | 1.512 (6) |
| O11A—C11A | 1.222 (6) | C41C—C51C | 1.530 (6) |
| O12A—C11A | 1.268 (6) | C2C—H2C | 0.9500 |
| O31A—N3A | 1.208 (5) | C4C—H4C | 0.9500 |
| O32A—N3A | 1.226 (5) | C5C—H5C | 0.9500 |
| O51A—N5A | 1.236 (6) | C6C—H6C | 0.9500 |
| O52A—N5A | 1.221 (6) | C11C—H14C | 0.9800 |
| Bond                  | Length (Å) | Bond                  | Length (Å) |
|----------------------|------------|----------------------|------------|
| O12A—H12A            | 0.8400     | C11C—H12C            | 0.9800     |
| N3B—C3B              | 1.454 (5)  | C11C—H13C            | 0.9800     |
| N5B—C5B              | 1.457 (5)  | C21C—H21C            | 1.0000     |
| N3A—C3A              | 1.470 (5)  | C31C—H32C            | 0.9900     |
| N5A—C5A              | 1.462 (5)  | C31C—H31C            | 0.9900     |
| N1C—C6C              | 1.333 (6)  | C41C—H41C            | 0.9900     |
| N1C—C2C              | 1.338 (5)  | C41C—H42C            | 0.9900     |
| N11C—C11C            | 1.485 (5)  | C51C—H52C            | 0.9900     |
| N11C—C21C            | 1.512 (4)  | C51C—H51C            | 0.9900     |
| N11C—C31C            | 1.488 (5)  | C2D—C3D              | 1.386 (5)  |
| N11C—H11C            | 0.9300     | C3D—C21D             | 1.499 (5)  |
| N1D—C2D              | 1.330 (5)  | C3D—C4D              | 1.362 (5)  |
| N1D—C6D              | 1.337 (5)  | C4D—C5D              | 1.372 (6)  |
| N11D—C51D            | 1.499 (5)  | C5D—C6D              | 1.381 (5)  |
| N11D—C11D            | 1.469 (5)  | C21D—C31D            | 1.504 (5)  |
| N11D—C21D            | 1.512 (4)  | C31D—C41D            | 1.513 (7)  |
| N11D—H11D            | 0.9300     | C41D—C51D            | 1.501 (7)  |
| C1B—C6B              | 1.390 (6)  | C2D—H2D              | 0.9500     |
| C1B—C11B             | 1.481 (6)  | C4D—H4D              | 0.9500     |
| C1B—C2B              | 1.404 (5)  | C5D—H5D              | 0.9500     |
| C2B—C3B              | 1.414 (5)  | C6D—H6D              | 0.9500     |
| C3B—C4B              | 1.364 (5)  | C11D—H12D            | 0.9800     |
| C4B—C5B              | 1.366 (5)  | C11D—H13D            | 0.9800     |
| C5B—C6B              | 1.408 (5)  | C11D—H14D            | 0.9800     |
| C2B—H2B              | 0.9500     | C21D—H21D            | 1.0000     |
| C4B—H4B              | 0.9500     | C31D—H31D            | 0.9900     |
| C6B—H6B              | 0.9500     | C31D—H32D            | 0.9900     |
| C1A—C6A              | 1.353 (5)  | C41D—H41D            | 0.9900     |
| C1A—C2A              | 1.432 (5)  | C41D—H42D            | 0.9900     |
| C1A—C11A             | 1.468 (6)  | C51D—H51D            | 0.9900     |
| C2A—C3A              | 1.414 (5)  | C51D—H52D            | 0.9900     |
| C3A—C4A              | 1.379 (5)  |                       |            |
| C11B—O11B—H11B       | 109.00     | C3C—C21C—C51C        | 118.1 (3)  |
| C11B—O12B—H12B       | 110.00     | N11C—C21C—C51C       | 102.9 (3)  |
| C11A—O12A—H12A       | 109.00     | N11C—C31C—C41C       | 104.6 (3)  |
| O31B—N3B—O32B        | 122.9 (4)  | C31C—C41C—C51C       | 106.4 (3)  |
| O31B—N3B—C3B         | 118.5 (3)  | C21C—C51C—C41C       | 105.6 (3)  |
| O32B—N3B—C3B         | 118.6 (3)  | N1C—C2C—H2C          | 118.00     |
| O52B—N5B—C5B         | 118.4 (3)  | C3C—C2C—H2C          | 119.00     |
| O51B—N5B—O52B        | 123.6 (4)  | C5C—C4C—H4C          | 120.00     |
| O51B—N5B—C5B         | 118.0 (3)  | C3C—C4C—H4C          | 120.00     |
| O32A—N3A—C3A         | 116.3 (3)  | C4C—C5C—H5C          | 121.00     |
| O31A—N3A—C3A         | 120.6 (4)  | C6C—C5C—H5C          | 121.00     |
| O31A—N3A—O32A        | 123.1 (4)  | C5C—C6C—H6C          | 118.00     |
| O51A—N5A—O52A        | 123.6 (4)  | N1C—C6C—H6C          | 118.00     |
| O52A—N5A—C5A         | 118.1 (4)  | N11C—C11C—H13C       | 110.00     |
| O51A—N5A—C5A         | 118.3 (4)  | H12C—C11C—H13C       | 109.00     |
| Bond                  | Angle (°) | Torsion (°) |
|-----------------------|-----------|-------------|
| C2C—N1C—C6C          | 117.6 (4) | N11C—C11C—H12C 109.00 |
| C11C—N11C—C21C       | 114.4 (3) | H13C—C11C—H14C 110.00 |
| C11C—N11C—C31C       | 114.4 (3) | N11C—C11C—H14C 110.00 |
| C21C—N11C—C31C       | 104.2 (3) | H12C—C11C—H14C 109.00 |
| C21C—N11C—H11C       | 108.00    | C51C—C21C—H21C 108.00 |
| C11C—N11C—H11C       | 108.00    | C3C—C21C—H21C 108.00 |
| C31C—N11C—H11C       | 108.00    | N11C—C21C—H21C 108.00 |
| C21C—N11C—C6D        | 117.5 (3) | C41C—C31C—H32C 111.00 |
| C21D—N11D—C51D       | 104.2 (3) | N11C—C31C—H31C 111.00 |
| C11D—N11D—C51D       | 114.6 (3) | C41C—C31C—H31C 111.00 |
| C11D—N11D—C21D       | 114.3 (3) | H31C—C31C—H32C 109.00 |
| C51D—N11D—H11D       | 108.00    | N11C—C31C—H32C 111.00 |
| C21D—N11D—H11D       | 108.00    | C51C—C41C—H41C 110.00 |
| C11D—N11D—H11D       | 108.00    | H41C—C41C—H42C 109.00 |
| C2B—C1B—C6B          | 121.4 (3) | C31C—C41C—H42C 110.00 |
| C2B—C1B—C11B         | 121.5 (4) | C31C—C41C—H41C 110.00 |
| C6B—C1B—C11B         | 117.2 (4) | C51C—C41C—H42C 110.00 |
| C1B—C2B—C3B          | 117.1 (3) | H51C—C51C—H52C 109.00 |
| O2B—C2B—C3B          | 125.7 (4) | C21C—C51C—H51C 111.00 |
| O2B—C2B—C1B          | 117.2 (3) | C41C—C51C—H52C 111.00 |
| N3B—C3B—C2B          | 120.6 (3) | C41C—C51C—H51C 111.00 |
| N3B—C3B—C4B          | 117.3 (3) | C21C—C51C—H52C 111.00 |
| C2B—C3B—C4B          | 122.1 (3) | N1D—C2D—C3D 123.8 (4) |
| C3B—C4B—C5B          | 119.7 (3) | C2D—C3D—C21D 121.6 (3) |
| N5B—C5B—C6B          | 119.7 (3) | C2D—C3D—C4D 117.2 (3) |
| C4B—C5B—C6B          | 121.2 (4) | C4D—C3D—C21D 121.2 (3) |
| N5B—C5B—C4B          | 119.0 (3) | C3D—C4D—C5D 120.8 (3) |
| O21B—C6B—C5B         | 127.0 (7) | C4D—C5D—C6D 118.0 (4) |
| C1B—C6B—C5B          | 118.5 (3) | N1D—C6D—C5D 122.8 (4) |
| O21B—C6B—C1B         | 114.1 (6) | C3D—C21D—C31D 118.3 (3) |
| O12B—C11B—C1B        | 116.6 (4) | N11D—C21D—C31D 112.0 (3) |
| O11B—C11B—O12B       | 122.0 (5) | N11D—C21D—C31D 103.0 (3) |
| O11B—C11B—C1B        | 121.4 (5) | C21D—C31D—C41D 105.6 (3) |
| C3B—C2B—H2B          | 121.00    | C31D—C41D—C51D 107.2 (4) |
| C1B—C2B—H2B          | 122.00    | N11D—C51D—C41D 104.8 (4) |
| C5B—C4B—H4B          | 120.00    | N1D—C2D—H2D 118.00 |
| C3B—C4B—H4B          | 120.00    | C3D—C2D—H2D 118.00 |
| C5B—C6B—H6B          | 121.00    | C3D—C4D—H4D 120.00 |
| C1B—C6B—H6B          | 121.00    | C5D—C4D—H4D 120.00 |
| C2A—C1A—C11A         | 120.4 (3) | C4D—C5D—H5D 121.00 |
| C2A—C1A—C6A          | 120.6 (4) | C6D—C5D—H5D 121.00 |
| C6A—C1A—C11A         | 119.0 (4) | N1D—C6D—H6D 119.00 |
| C1A—C2A—C3A          | 116.2 (3) | C5D—C6D—H6D 119.00 |
| O2A—C2A—C3A          | 124.2 (4) | N11D—C11D—H12D 109.00 |
| O2A—C2A—C1A          | 119.7 (4) | N11D—C11D—H13D 109.00 |
| N3A—C3A—C2A          | 119.9 (3) | N11D—C11D—H14D 109.00 |
| N3A—C3A—C4A          | 116.6 (3) | H12D—C11D—H13D 109.00 |
| C2A—C3A—C4A          | 123.5 (3) | H12D—C11D—H14D 110.00 |
| Bond/Angle/Dihedral | Value 1 | Value 2 | Value 3 | Value 4 | Value 5 | Value 6 |
|---------------------|---------|---------|---------|---------|---------|---------|
| C3A—C4A—C5A        | 116.6   |        |         |         |         |         |
| C4A—C5A—C6A        | 122.7   |        |         |         |         |         |
| N5A—C5A—C4A        | 117.7   |        |         |         |         |         |
| N5A—C5A—C6A        | 119.6   |        |         |         |         |         |
| C1A—C6A—C5A        | 120.5   |        |         |         |         |         |
| O11A—C11A—O12A     | 121.2   |        |         |         |         |         |
| O11A—C11A—C1A      | 121.1   |        |         |         |         |         |
| O12A—C11A—C1A      | 117.7   |        |         |         |         |         |
| C3A—C4A—H4A        | 122.0   |        |         |         |         |         |
| C5A—C4A—H4A        | 122.0   |        |         |         |         |         |
| C5A—C6A—H6A        | 120.0   |        |         |         |         |         |
| C1A—C6A—H6A        | 120.0   |        |         |         |         |         |
| N1C—C2C—C3C        | 123.1   |        |         |         |         |         |
| C2C—C3C—C4C        | 118.1   |        |         |         |         |         |
| C4C—C3C—C21C       | 121.0   |        |         |         |         |         |
| C2C—C3C—C21C       | 120.8   |        |         |         |         |         |
| C3C—C4C—C5C        | 119.1   |        |         |         |         |         |
| C4C—C5C—C6C        | 118.5   |        |         |         |         |         |
| N1C—C6C—C5C        | 123.5   |        |         |         |         |         |
| N11C—C21C—C3C      | 111.7   |        |         |         |         |         |
| O32B—N3B—C3B—C2B   | 173.7   |        |         |         |         |         |
| O31B—N3B—C3B—C4B   | 175.0   |        |         |         |         |         |
| O32B—N3B—C3B—C4B   | −5.0    |        |         |         |         |         |
| O31B—N3B—C3B—C2B   | −6.3    |        |         |         |         |         |
| O52B—N5B—C5B—C6B   | 5.0     |        |         |         |         |         |
| O52B—N5B—C5B—C4B   | −177.7  |        |         |         |         |         |
| O51B—N5B—C5B—C6B   | −175.7  |        |         |         |         |         |
| O51B—N5B—C5B—C4B   | 1.7     |        |         |         |         |         |
| O31A—N3A—C3A—C2A   | 5.8     |        |         |         |         |         |
| O31A—N3A—C3A—C4A   | −175.1  |        |         |         |         |         |
| O32A—N3A—C3A—C2A   | −174.6  |        |         |         |         |         |
| O32A—N3A—C3A—C4A   | 4.5     |        |         |         |         |         |
| O51A—N5A—C5A—C6A   | 174.3   |        |         |         |         |         |
| O52A—N5A—C5A—C6A   | −4.9    |        |         |         |         |         |
| O51A—N5A—C5A—C4A   | −4.7    |        |         |         |         |         |
| O52A—N5A—C5A—C4A   | 176.0   |        |         |         |         |         |
| C2C—N1C—C6C—C5C    | −0.2    |        |         |         |         |         |
| C6C—N1C—C2C—C3C    | 0.3     |        |         |         |         |         |
| C31C—N11C—C21C—C3C | 168.2   |        |         |         |         |         |
| C31C—N11C—C21C—C51C| 40.5    |        |         |         |         |         |
| C11C—N11C—C21C—C3C | −66.1   |        |         |         |         |         |
| C11C—N11C—C31C—C41C| −162.7  |        |         |         |         |         |
| C11C—N11C—C21C—C51C| 166.3   |        |         |         |         |         |
| C21C—N11C—C31C—C41C| −36.9   |        |         |         |         |         |
| C6D—N1D—C2D—C3D    | −0.5    |        |         |         |         |         |
| C2D—N1D—C6D—C5D    | 1.8     |        |         |         |         |         |
| C21D—N11D—C51D—C41D| −33.4   |        |         |         |         |         |
C51D—N11D—C21D—C31D 39.4 (4)  C4C—C3C—C21C—C51C −134.4 (4)
C11D—N11D—C21D—C3D −66.6 (4)  C2C—C3C—C4C—C5C −1.6 (5)
C11D—N11D—C21D—C31D 165.2 (4)  C21C—C3C—C4C—C5C 179.9 (3)
C51D—N11D—C21D—C3D 167.6 (3)  C3C—C4C—C5C—C6C 1.8 (6)
C11D—N11D—C51D—C41D −159.0 (4)  C4C—C5C—C6C—N1C −0.9 (6)
C6B—C1B—C11B—O11B −4.3 (6)  C3C—C21C—C51C—C41C −129.0 (4)
C11B—C1B—C2B—C3B −180.0 (3)  C3C—C21C—C51C—C41C 18.9 (5)
C11B—C1B—C2B—O2B 0.6 (5)  C3C—C21C—C51C—C41C −154.1 (4)
C2B—C1B—C11B—O2B −2.5 (6)  C21D—C3D—C4D—C5D 179.0 (3)
C6B—C1B—C2B—C3B 0.9 (5)  C4D—C3D—C21D—C31D 50.8 (5)
C11B—C1B—C6B—C5B −178.3 (3)  C4D—C3D—C21D—N11D −68.8 (4)
C2B—C1B—C6B—C5B 0.9 (5)  C21D—C3D—C21D—C31D 111.4 (4)
C1B—C2B—C3B—C4B −2.6 (5)  C21D—C3D—C21D—C31D 0.1 (5)
C1B—C2B—C3B—N3B 179.9 (3)  C21D—C3D—C21D—C31D 111.4 (4)
C1B—C2B—C3B—O12B 179.6 (4)  C3C—C21C—C51C—C41C 1.8 (6)
C1B—C2B—C3B—O2B −17.8 (3)  C3C—C21C—C51C—C41C −28.2 (4)
C3B—C4B—C5B—N5B −177.7 (3)  C3C—C21C—C51C—C41C 18.9 (5)
C3B—C4B—C5B—C6B −0.4 (5)  C3C—C21C—C51C—C41C −154.1 (4)
C3B—C4B—C5B—C6B 0.9 (5)  C3C—C21C—C51C—C41C 18.9 (5)

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A   | D—H···A |
|-------------|------|-------|---------|---------|
| O12A—H12A···O2A | 0.84 | 1.71  | 2.475 (4) | 150     |
| O12B—H12B···O2B | 0.84 | 1.63  | 2.411 (4) | 152     |
| N11C—H11C···N1D | 0.93 | 1.89  | 2.809 (4) | 169     |
| N11D—H11D···N1C | 0.93 | 1.90  | 2.817 (5) | 168     |
| N11D—H11D···N1C | 0.93 | 1.90  | 2.817 (5) | 168     |
| C2C—H2C···O11A | 0.95 | 2.42  | 3.228 (5) | 143     |
| C4C—H4C···O31A | 0.95 | 2.59  | 3.452 (5) | 151     |
| C5D—H5D···O31B | 0.95 | 2.46  | 3.071 (5) | 122     |
| C6C—H6C···O32A | 0.95 | 2.27  | 3.054 (5) | 139     |
| C6D—H6D···O31B | 0.95 | 2.55  | 3.136 (5) | 120     |
| C11C—H13C···O32B | 0.98 | 2.48  | 3.151 (6) | 126     |
| C11D—H14D···O51A | 0.98 | 2.55  | 3.373 (6) | 141     |
| C21C—H21C···O2A | 1.00 | 2.27  | 3.163 (5) | 148     |
| C21D—H21D···O11B | 1.00 | 2.44  | 3.307 (5) | 144     |
| C51C—H52C···O11A | 0.99 | 2.54  | 3.534 (6) | 177     |

Symmetry codes: (i) x+1, y, z; (ii) −x+1, y+1/2, −z+1/2; (iii) x+1/2, −y+1/2, −z; (iv) x+1, y+1, z; (v) x, y+1, z.
(II) (1R,2S)-1-Methyl-2-(pyridin-3-yl)pyrrolidin-1-ium 3-carboxy-4-hydroxybenzenesulfonate

Crystal data

C₁₀H₁₅N₂⁺·C₇H₅O₆S⁻

\( M_r = 380.41 \)

Monoclinic, \( P 2_1 \)

Hall symbol: P 2yb

\( a = 7.1568 (3) \) Å

\( b = 12.6416 (5) \) Å

\( c = 19.1519 (8) \) Å

\( \beta = 93.729 (4)° \)

\( V = 1729.07 (12) \) Å³

\( Z = 4 \)

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

\( \omega \) scans

Absorption correction: multi-scan

(CrysAlis PRO; Agilent, 2013)

\( T_{\text{min}} = 0.909, T_{\text{max}} = 0.981 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R(F^2 > 2\sigma(F^2)) = 0.046 \)

\( wR(F^2) = 0.108 \)

\( S = 1.01 \)

5104 reflections

469 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

\(\Delta / \sigma = 0.001 \)

\( \Delta \rho_{\text{max}} = 0.49 \) e Å⁻³

\( \Delta \rho_{\text{min}} = -0.36 \) e Å⁻³

Absolute structure: Flack (1983), 4361 Friedel pairs

Absolute structure parameter: −0.02 (9)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x   | y   | z   | U₁₁ | U₂₂ | U₃₃ |
|---|------|------|-----|-----|-----|-----|
| S5A | 0.68704 (12) | 0.55842 (7) | 0.41012 (4) | 0.0263 (3) |
| O2A | 0.3397 (4) | 0.3912 (2) | 0.14516 (12) | 0.0340 (8) |
| O11A | 0.3204 (4) | 0.2139 (2) | 0.32641 (13) | 0.0348 (8) |

Supporting information

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| Atom   | U1   | U2   | U3   | U12  |
|--------|------|------|------|-------|
| O12A   | 0.2584 (4) | 0.2236 (2) | 0.21069 (13) | 0.0337 (8) |
| O51A   | 0.8728 (4) | 0.5131 (3) | 0.41339 (15) | 0.0508 (10) |
| O52A   | 0.6922 (4) | 0.6735 (2) | 0.40180 (14) | 0.0422 (9) |
| O53A   | 0.5792 (4) | 0.5253 (2) | 0.46723 (12) | 0.0393 (9) |
| C1A    | 0.4129 (4) | 0.3676 (3) | 0.26886 (17) | 0.0221 (9) |
| C2A    | 0.4124 (5) | 0.4284 (3) | 0.20674 (17) | 0.0222 (10) |
| C3A    | 0.4845 (5) | 0.5304 (3) | 0.20917 (17) | 0.0240 (10) |
| C4A    | 0.5643 (4) | 0.5705 (3) | 0.27120 (17) | 0.0239 (9) |
| C5A    | 0.5696 (4) | 0.5108 (3) | 0.33217 (17) | 0.0211 (9) |
| C6A    | 0.4930 (5) | 0.4106 (3) | 0.33044 (18) | 0.0234 (10) |
| C11A   | 0.3243 (5) | 0.2614 (3) | 0.26686 (19) | 0.0259 (11) |
| S5B    | 0.30149 (14) | −0.14181 (8) | 0.08257 (5) | 0.0345 (3) |
| O2B    | 0.6834 (4) | 0.0076 (2) | 0.34578 (12) | 0.0344 (8) |
| O11B   | 0.7029 (4) | 0.1928 (2) | 0.16767 (13) | 0.0347 (8) |
| O12B   | 0.7680 (4) | 0.1780 (2) | 0.28273 (13) | 0.0335 (8) |
| O51B   | 0.1062 (4) | −0.1205 (3) | 0.09470 (17) | 0.0625 (11) |
| O52B   | 0.3307 (4) | −0.2529 (2) | 0.07618 (16) | 0.0480 (10) |
| O53B   | 0.3571 (6) | −0.0759 (3) | 0.02651 (16) | 0.0801 (15) |
| C1B    | 0.6053 (4) | 0.0375 (3) | 0.22345 (17) | 0.0206 (9) |
| C2B    | 0.6058 (5) | −0.0256 (3) | 0.28333 (17) | 0.0233 (10) |
| C3B    | 0.5299 (5) | −0.1274 (3) | 0.28007 (18) | 0.0255 (10) |
| C4B    | 0.4433 (5) | −0.1631 (3) | 0.21848 (19) | 0.0261 (10) |
| C5B    | 0.4331 (5) | −0.0982 (3) | 0.15869 (17) | 0.0231 (10) |
| C6B    | 0.5145 (4) | 0.0004 (3) | 0.16130 (17) | 0.0222 (10) |
| C11B   | 0.6976 (5) | 0.1427 (3) | 0.22658 (19) | 0.0260 (11) |
| N1C    | 0.8536 (4) | 0.3758 (3) | 0.18074 (15) | 0.0270 (9) |
| N11C   | 0.9801 (4) | 0.5668 (3) | −0.00002 (14) | 0.0295 (9) |
| C2C    | 0.8558 (5) | 0.4408 (3) | 0.12534 (19) | 0.0253 (10) |
| C3C    | 0.9371 (4) | 0.5393 (3) | 0.12903 (18) | 0.0257 (10) |
| C4C    | 1.0161 (5) | 0.5724 (3) | 0.19371 (18) | 0.0294 (10) |
| C5C    | 1.0065 (5) | 0.5074 (3) | 0.25102 (18) | 0.0296 (11) |
| C6C    | 0.9288 (5) | 0.4092 (3) | 0.24258 (19) | 0.0297 (11) |
| C11C   | 1.1769 (5) | 0.5314 (4) | −0.0030 (2) | 0.0392 (14) |
| C21C   | 0.9336 (5) | 0.6148 (3) | 0.06816 (18) | 0.0290 (11) |
| C31C   | 0.7439 (6) | 0.6662 (4) | 0.0489 (2) | 0.0493 (16) |
| C41C   | 0.7621 (7) | 0.7097 (4) | −0.0242 (2) | 0.0529 (17) |
| C51C   | 0.9232 (6) | 0.6511 (4) | −0.0534 (2) | 0.0476 (16) |
| N1D    | 0.1735 (4) | 0.0297 (2) | 0.31881 (15) | 0.0257 (8) |
| N11D   | −0.0524 (4) | −0.2131 (3) | 0.48368 (14) | 0.0327 (10) |
| C2D    | 0.1839 (5) | −0.0236 (3) | 0.37895 (18) | 0.0239 (10) |
| C3D    | 0.1071 (4) | −0.1235 (3) | 0.38558 (16) | 0.0211 (9) |
| C4D    | 0.0196 (5) | −0.1695 (3) | 0.32573 (17) | 0.0256 (10) |
| C5D    | 0.0119 (5) | −0.1153 (3) | 0.26338 (18) | 0.0283 (11) |
| C6D    | 0.0898 (5) | −0.0152 (3) | 0.26175 (19) | 0.0284 (11) |
| C11D   | −0.1872 (6) | −0.1290 (4) | 0.4998 (2) | 0.0430 (14) |
| C21D   | 0.1287 (5) | −0.1769 (3) | 0.45539 (17) | 0.0267 (10) |
| C31D   | 0.2434 (6) | −0.2778 (4) | 0.4595 (2) | 0.0442 (14) |
| C41D   | 0.1992 (8) | −0.3244 (4) | 0.5301 (2) | 0.0626 (19) |
### Atomic displacement parameters (Å²)

|   | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|---|------|------|------|------|------|------|
| S5A | 0.0295 (4) | 0.0253 (5) | 0.0232 (4) | −0.0031 (4) | −0.0062 (3) | 0.0026 (4) |
| O2A | 0.0467 (15) | 0.0280 (15) | 0.0261 (13) | −0.0022 (13) | −0.0058 (11) | −0.0012 (11) |
| O11A | 0.0456 (15) | 0.0234 (14) | 0.0352 (14) | −0.0115 (13) | 0.0018 (11) | 0.0042 (12) |

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### Supporting Information

|   | O12A | O13A | O14A | O15A | O16A |
|---|------|------|------|------|------|
|   | 0.0397 (14) | 0.0249 (14) | 0.0360 (14) | -0.0065 (13) | -0.0013 (11) |
|   | 0.0347 (14) | 0.073 (2) | 0.0424 (16) | 0.0124 (17) | -0.0146 (12) |
|   | 0.0580 (18) | 0.0242 (14) | 0.0417 (16) | -0.0116 (14) | -0.0180 (13) |
|   | 0.0496 (15) | 0.0460 (17) | 0.0219 (12) | -0.0115 (15) | -0.0002 (10) |
| C1A | 0.0201 (16) | 0.0212 (17) | 0.0249 (16) | 0.0028 (16) | 0.0010 (12) |
| C2A | 0.0238 (17) | 0.0227 (18) | 0.0197 (16) | 0.0035 (15) | -0.0009 (13) |
| C3A | 0.0271 (17) | 0.0256 (18) | 0.0193 (16) | 0.0050 (16) | 0.0008 (13) |
| C4A | 0.0213 (15) | 0.0197 (17) | 0.0305 (17) | -0.0002 (16) | 0.0009 (13) |
| C5A | 0.0221 (16) | 0.0196 (17) | 0.0210 (16) | -0.0011 (16) | -0.0025 (12) |
| C6A | 0.0264 (18) | 0.0203 (18) | 0.0233 (17) | 0.0010 (16) | 0.0002 (13) |
| C11A | 0.0231 (17) | 0.0221 (19) | 0.0326 (19) | 0.0001 (15) | 0.0022 (14) |
| S5B | 0.0201 (15) | 0.0212 (17) | 0.0249 (16) | -0.0116 (14) | -0.0180 (13) |
| O2B | 0.0499 (15) | 0.0292 (14) | 0.0227 (12) | -0.0051 (14) | -0.0078 (11) |
| O11B | 0.0440 (15) | 0.0269 (15) | 0.0330 (14) | -0.0111 (13) | 0.0007 (11) |
| O12B | 0.0442 (15) | 0.0270 (14) | 0.0286 (14) | -0.0052 (13) | -0.0029 (11) |
| O51B | 0.0379 (16) | 0.070 (2) | 0.075 (2) | -0.0237 (18) | -0.0305 (15) |
| O52B | 0.0379 (16) | 0.070 (2) | 0.075 (2) | -0.0237 (18) | -0.0305 (15) |
| O53B | 0.0379 (16) | 0.070 (2) | 0.075 (2) | -0.0237 (18) | -0.0305 (15) |

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Geometric parameters (Å, °)

| Bond                  | Length (Å) | Angle (°) | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|------------|-----------|
| S5A—O51A              | 1.445 (3)  |           | C3B—H3B    | 0.9500    |
| S5A—O52A              | 1.464 (3)  |           | C4B—H4B    | 0.9500    |
| S5A—O53A              | 1.441 (3)  |           | C6B—H6B    | 0.9500    |
| S5A—C5A               | 1.770 (3)  |           | C2C—C3C    | 1.374 (5) |
| S5B—O51B              | 1.457 (3)  |           | C3C—C21C   | 1.506 (5) |
| S5B—O52B              | 1.434 (3)  |           | C3C—C4C    | 1.392 (5) |
| S5B—O53B              | 1.436 (4)  |           | C4C—C5C    | 1.374 (5) |
| S5B—C5B               | 1.771 (4)  |           | C5C—C6C    | 1.375 (5) |
| O2A—C2A               | 1.343 (4)  |           | C21C—C31C  | 1.529 (6) |
| O11A—C11A             | 1.291 (4)  |           | C31C—C41C  | 1.518 (6) |
| O12A—C11A             | 1.242 (4)  |           | C31C—C51C  | 1.508 (7) |
| O2A—H2A               | 0.8400     |           | C2C—H2C    | 0.9500    |
| O11A—H11A             | 0.9500     |           | C4C—H4C    | 0.9500    |
| O2B—C2B               | 1.352 (4)  |           | C5C—H5A    | 0.9500    |
| O11B—C11B             | 1.297 (4)  |           | C6C—H6C    | 0.9500    |
| O12B—C11B             | 1.241 (4)  |           | C11C—H134  | 0.9800    |
| O2B—H2B               | 0.8400     |           | C11C—H12C  | 0.9800    |
| O11B—H11B             | 0.9500     |           | C11C—H13C  | 0.9800    |
| N1C—C6C               | 1.337 (5)  |           | C21C—H21C  | 1.0000    |
| N1C—C2C               | 1.343 (5)  |           | C31C—H32C  | 0.9900    |
| N11C—C11C             | 1.483 (5)  |           | C31C—H31C  | 0.9900    |
| N11C—C51C             | 1.514 (6)  |           | C41C—H41C  | 0.9900    |
| N11C—C21C             | 1.497 (5)  |           | C41C—H42C  | 0.9900    |
| N11C—H11C             | 0.9300     |           | C51C—H52C  | 0.9900    |
| N1D—C2D               | 1.332 (4)  |           | C51C—H51C  | 0.9900    |
| N1D—C6D               | 1.338 (5)  |           | C2D—C3D    | 1.386 (5) |
| N11D—C51D             | 1.503 (5)  |           | C3D—C21D   | 1.497 (5) |
| N11D—C11D             | 1.482 (6)  |           | C3D—C4D    | 1.397 (5) |
| N11D—C21D             | 1.508 (5)  |           | C4D—C5D    | 1.375 (5) |
| N11D—H11D             | 0.9300     |           | C5D—C6D    | 1.384 (5) |
| C1A—C2A               | 1.416 (5)  |           | C21D—C31D  | 1.516 (6) |
| C1A—C11A              | 1.484 (5)  |           | C31D—C41D  | 1.527 (6) |
| C1A—C6A               | 1.388 (5)  |           | C41D—C51D  | 1.506 (7) |
| C2A—C3A               | 1.389 (5)  |           | C2D—H2D    | 0.9500    |
| C3A—C4A               | 1.381 (5)  |           | C4D—H4D    | 0.9500    |
| C4A—C5A               | 1.389 (5)  |           | C5D—H5D    | 0.9500    |
| C5A—C6A               | 1.380 (5)  |           | C6D—H6D    | 0.9500    |
| C3A—H3A               | 0.9500     |           | C11D—H12D  | 0.9800    |
| C4A—H4A               | 0.9500     |           | C11D—H13D  | 0.9800    |
| C6A—H6A               | 0.9500     |           | C11D—H14D  | 0.9800    |
| C1B—C6B               | 1.399 (5)  |           | C21D—H21D  | 1.0000    |
| C1B—C11B              | 1.484 (5)  |           | C31D—H31D  | 0.9900    |
| C1B—C2B               | 1.397 (5)  |           | C31D—H32D  | 0.9900    |
| C2B—C3B               | 1.397 (5)  |           | C41D—H41D  | 0.9900    |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Distance (Å) |
|--------------|--------------|--------------|--------------|--------------|
| C3B—C4B      | 1.373 (5)    | C41D—H42D    | 0.9900       |
| C4B—C5B      | 1.407 (5)    | C51D—H51D    | 0.9900       |
| C5B—C6B      | 1.375 (5)    | C51D—H52D    | 0.9900       |
| O51A—S5A—O52A| 111.65 (19)  | N11C—C21C—C31C| 101.9 (3)   |
| O51A—S5A—O53A| 112.86 (17)  | C21C—C31C—C41C| 104.4 (3)   |
| O51A—S5A—C5A | 106.66 (17)  | C31C—C41C—C51C| 106.1 (4)   |
| O52A—S5A—O53A| 112.94 (16)  | N11C—C51C—C41C| 105.9 (3)   |
| O52A—S5A—C5A | 105.07 (17)  | N1C—C2C—H2C   | 119.00       |
| O53A—S5A—C5A | 107.03 (15)  | C3C—C2C—H2C   | 119.00       |
| O51B—S5B—C5B | 105.99 (18)  | C5C—C4C—H4C   | 120.00       |
| O51B—S5B—O52B| 111.8 (2)    | C3C—C4C—H4C   | 120.00       |
| O51B—S5B—O53B| 109.1 (2)    | C4C—C5C—H5A   | 121.00       |
| O53B—S5B—C5B | 106.1 (2)    | C6C—C5C—H5A   | 121.00       |
| O52B—S5B—O53B| 116.4 (2)    | C5C—C6C—H6C   | 119.00       |
| O52B—S5B—C5B | 106.70 (18)  | N1C—C6C—H6C   | 119.00       |
| C2A—O2A—H2A | 109.00       | N11C—C11C—H13C| 109.00       |
| C11A—O11A—H11A| 113.00       | H12C—C11C—H13C| 109.00       |
| C2B—O2B—H2B | 109.00       | N11C—C11C—H12C| 109.00       |
| C11B—O11B—H11B| 112.00       | H13C—C11C—H134| 109.00       |
| C2C—N1C—C6C | 118.8 (4)    | N11C—C11C—H134| 109.00       |
| C11C—N11C—C21C| 114.9 (3)    | H12C—C11C—H134| 109.00       |
| C11C—N11C—C51C| 113.6 (3)    | C31C—C21C—H21C| 108.00       |
| C21C—N11C—C51C| 103.8 (3)    | C3C—C21C—H21C | 108.00       |
| C51C—N11C—H11C| 108.00       | N11C—C21C—H21C| 108.00       |
| C21C—N11C—H11C| 108.00       | C41C—C31C—H32C| 111.00       |
| C11C—N11C—H11C| 108.00       | C21C—C31C—H31C| 111.00       |
| C2D—N1D—C6D | 119.2 (3)    | C41C—C31C—H31C| 111.00       |
| C11D—N11D—C51D| 114.2 (3)    | H31C—C31C—H32C| 109.00       |
| C11D—N11D—C21D| 116.3 (3)    | C21C—C31C—H32C| 111.00       |
| C21D—N11D—C51D| 103.6 (3)    | C51C—C41C—H41C| 110.00       |
| C51D—N11D—H11D| 107.00       | H41C—C41C—H42C| 109.00       |
| C11D—N11D—H11D| 107.00       | C31C—C41C—H42C| 111.00       |
| C21D—N11D—H11D| 107.00       | C31C—C41C—H41C| 110.00       |
| C6A—C1A—C11A| 121.9 (3)    | C51C—C41C—H42C| 110.00       |
| C2A—C1A—C11A | 119.4 (3)    | H51C—C51C—H52C| 109.00       |
| C2A—C1A—C6A | 118.7 (3)    | N11C—C51C—H51C| 111.00       |
| O2A—C2A—C1A | 121.8 (3)    | C41C—C51C—H52C| 111.00       |
| O2A—C2A—C3A | 118.5 (3)    | C41C—C51C—H51C| 111.00       |
| C1A—C2A—C3A | 119.7 (3)    | N11C—C51C—H52C| 111.00       |
| C2A—C3A—C4A | 120.1 (3)    | N1D—C2D—C3D   | 122.7 (3)    |
| C3A—C4A—C5A | 120.7 (3)    | C2D—C3D—C21D  | 118.3 (3)    |
| C4A—C5A—C6A | 119.3 (3)    | C2D—C3D—C4D   | 117.6 (3)    |
| S5A—C5A—C4A | 120.7 (3)    | C4D—C3D—C21D  | 124.1 (3)    |
| S5A—C5A—C6A | 119.9 (3)    | C3D—C4D—C5D   | 119.7 (3)    |
| C1A—C6A—C5A | 121.4 (3)    | C4D—C5D—C6D   | 118.8 (3)    |
| O11A—C11A—C1A | 115.6 (3)    | N1D—C6D—C5D   | 121.9 (3)    |
| O12A—C11A—C1A | 120.5 (3)    | C3D—C21D—C31D | 116.7 (3)    |
| Bond                  | Angle (°)  | Bond                  | Angle (°)  |
|----------------------|------------|----------------------|------------|
| O11A—C11A—O12A      | 123.9 (3)  | N11D—C21D—C3D       | 114.6 (3)  |
| C2A—C3A—H3A         | 120.00     | N11D—C21D—C31D      | 101.6 (3)  |
| C4A—C3A—H3A         | 120.00     | C21D—C31D—C41D      | 103.2 (3)  |
| C3A—C4A—H4A         | 120.00     | C31D—C41D—C51D      | 105.7 (4)  |
| C5A—C4A—H4A         | 120.00     | N11D—C51D—C41D      | 106.4 (3)  |
| C5A—C6A—H6A         | 119.00     | N1D—C2D—H2D         | 119.00     |
| C1A—C6A—H6A         | 119.00     | C3D—C2D—H2D         | 119.00     |
| C6B—C1B—C11B        | 121.0 (3)  | C3D—C4D—H4D         | 120.00     |
| C2B—C1B—C11B        | 120.1 (3)  | C5D—C4D—H4D         | 120.00     |
| C2B—C1B—C6B         | 118.9 (3)  | C4D—C5D—H5D         | 121.00     |
| C1B—C2B—C3B         | 120.6 (3)  | C6D—C5D—H5D         | 121.00     |
| O2B—C2B—C3B         | 117.5 (3)  | N1D—C6D—H6D         | 119.00     |
| O2B—C2B—C1B         | 121.9 (3)  | C5D—C6D—H6D         | 119.00     |
| C2B—C3B—C4B         | 119.6 (3)  | N11D—C11D—H12D      | 109.00     |
| C3B—C4B—C5B         | 120.3 (3)  | N11D—C11D—H13D      | 110.00     |
| C4B—C5B—C6B         | 120.0 (3)  | N11D—C11D—H14D      | 109.00     |
| S5B—C5B—C4B         | 119.0 (3)  | H12D—C11D—H13D      | 109.00     |
| S5B—C5B—C6B         | 120.9 (3)  | H12D—C11D—H14D      | 109.00     |
| C1B—C6B—C5B         | 120.5 (3)  | H13D—C11D—H14D      | 109.00     |
| O12B—C11B—C1B       | 120.8 (3)  | N11D—C21D—H21D      | 108.00     |
| O11B—C11B—C1B       | 116.1 (3)  | C3D—C21D—H21D       | 108.00     |
| O11B—C11B—O12B      | 123.1 (3)  | C3D—C21D—H21D       | 108.00     |
| C2B—C3B—H3B         | 120.00     | C21D—C31D—H31D      | 111.00     |
| C4B—C3B—H3B         | 120.00     | C21D—C31D—H32D      | 111.00     |
| C3B—C4B—H4B         | 120.00     | C41D—C31D—H31D      | 111.00     |
| C5B—C4B—H4B         | 120.00     | C41D—C31D—H32D      | 111.00     |
| C5B—C6B—H6B         | 120.00     | H31D—C31D—H32D      | 109.00     |
| C1B—C6B—H6B         | 120.00     | C31D—C41D—H41D      | 111.00     |
| N1C—C2C—C3C         | 122.7 (3)  | C31D—C41D—H42D      | 111.00     |
| C2C—C3C—C4C         | 117.7 (3)  | C51D—C41D—H41D      | 111.00     |
| C4C—C3C—C21C        | 118.9 (3)  | C51D—C41D—H42D      | 111.00     |
| C2C—C3C—C21C        | 123.3 (3)  | H41D—C41D—H42D      | 109.00     |
| C3C—C4C—C5C         | 119.9 (3)  | N11D—C51D—H51D      | 110.00     |
| C4C—C5C—C6C         | 118.8 (3)  | N11D—C51D—H52D      | 111.00     |
| N1C—C6C—C5C         | 122.1 (3)  | C41D—C51D—H51D      | 110.00     |
| N11C—C21C—C3C       | 115.2 (3)  | C41D—C51D—H52D      | 110.00     |
| C3C—C21C—C31C       | 115.2 (3)  | H51D—C51D—H52D      | 109.00     |
| O51A—S5A—C5A—C4A    | −95.6 (3)  | C6B—C1B—C2B—O2B     | −176.9 (3) |
| O51A—S5A—C5A—C6A    | 80.1 (3)   | C6B—C1B—C2B—C3B     | 5.0 (5)    |
| O52A—S5A—C5A—C4A    | 23.0 (3)   | C11B—C1B—C2B—C3B    | −175.9 (3) |
| O52A—S5A—C5A—C6A    | −161.3 (3) | C2B—C1B—C6B—C5B     | −2.3 (5)   |
| O53A—S5A—C5A—C4A    | 143.4 (3)  | C11B—C1B—C6B—C5B    | 178.6 (3)  |
| O53A—S5A—C5A—C6A    | −41.0 (3)  | C2B—C1B—C11B—O11B   | 175.1 (3)  |
| O53B—S5B—C5B—C6B    | 19.4 (4)   | C2B—C1B—C11B—O12B   | −3.5 (5)   |
| O52B—S5B—C5B—C4B    | −40.0 (3)  | C6B—C1B—C11B—O11B   | −5.8 (5)   |
| O51B—S5B—C5B—C4B    | 79.3 (3)   | C11B—C1B—C2B—O2B    | 2.2 (5)    |
| O51B—S5B—C5B—C6B    | −96.5 (3)  | C6B—C1B—C11B—O12B   | 175.6 (3)  |
Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H  | H···A  | D···A  | D—H···A  |
|------------------|-------|--------|--------|----------|
| O2A—H2A···O12A   | 0.84  | 1.80   | 2.549 (4) | 147      |
| O2B—H2B···O12B   | 0.84  | 1.82   | 2.561 (4) | 146      |
| O11A—H11A···N1D  | 0.95  | 1.60   | 2.555 (4) | 179      |
| O11B—H11B···N1C  | 0.95  | 1.61   | 2.558 (4) | 179      |
| N11C—H11C···O51B  | 0.93  | 2.32   | 3.022 (5) | 132      |
| N11C—H11C···O53B  | 0.93  | 2.15   | 3.029 (5) | 157      |
| N11D—H11D···O52A  | 0.93  | 1.85   | 2.735 (4) | 158      |
| C11D—H12D···O2B  | 0.98  | 2.51   | 3.491 (5) | 174      |
| C2C—H2C···O53B   | 0.95  | 2.29   | 3.201 (5) | 160      |
|                  | d (Å) | e (Å) | d (Å)  |    |
|------------------|-------|-------|--------|----|
| C2D—H2D···O53A\textsuperscript{iv} | 0.95  | 2.45  | 3.359 (4) | 160 |
| C4A—H4A···O52A  | 0.95  | 2.54  | 2.914 (4) | 103 |
| C6B—H6B···O53B  | 0.95  | 2.54  | 2.913 (5) | 103 |
| C11C—H12C···O2A\textsuperscript{v} | 0.98  | 2.52  | 3.481 (5) | 165 |
| C11C—H13C···O52B\textsuperscript{vi} | 0.98  | 2.46  | 3.290 (5) | 142 |
| C11D—H13D···O51A\textsuperscript{v} | 0.98  | 2.37  | 3.251 (5) | 150 |
| C21C—H21C···O52B\textsuperscript{vi} | 1.00  | 2.42  | 3.331 (5) | 151 |

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