

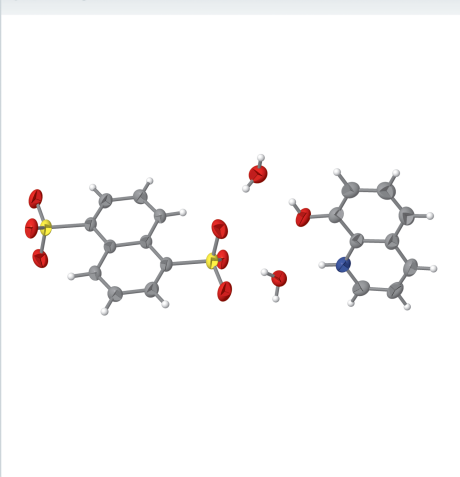
Bis(8-hydroxyquinolinium) naphthalene-1,5-disulfonate tetrahydrate

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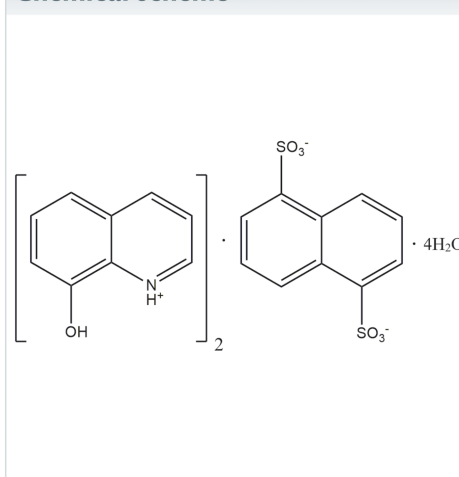
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The interaction between 8-hydroxyquinoline (8HQ, C₉H₇NO) and naphthalene-1,5-disulfonic acid (H₂NDS, C₁₀H₈O₆S₂) in aqueous media results in the formation of the salt hydrate bis(8-hydroxyquinolinium) naphthalene-1,5-disulfonate tetrahydrate, 2C₉H₈NO⁺·C₁₀H₆O₆S₂²⁻·4H₂O. The asymmetric unit comprises one protonated 8HQ⁺ cation, half of an NDS²⁻ dianion symmetrically disposed around a center of inversion, and two water molecules. Within the crystal structure, these components are organized into chains along the [010] and [10 $\bar{1}$] directions through O—H···O and N—H···O hydrogen-bonding interactions, forming a di-periodic network parallel to (101). Additional stabilizing interactions such as C—H···O, C—H··· π , and π – π interactions extend this arrangement into a tri-periodic network structure

3D view



Chemical scheme



Structure description

8-Hydroxyquinoline (8HQ, C₉H₇NO, HL), known also as oxine, is a bidentate chelating agent. It forms three species: H₂L⁺, HL and L⁻. 8HQ bearing a hetero-nitrogen atom (pK_a = 10.8) and the 8-substituted phenol group (pK_a = 4.9) is a good organic acid–base adduct conformer and has been reported to form supramolecularly organized compounds with acidic counter parts under formation of multiple hydrogen bonds (Smith *et al.*, 2003). 8HQ is used in analytical chemistry for the quantitative determination of metal ions because the resulting complexes are insoluble in water. The aluminium complex (Cölle *et al.*, 2002; Katakura & Koide, 2006) is a common component of organic light-emitting diodes (OLEDs). Substituents on the quinoline ring result in compounds with luminescence properties (Montes *et al.*, 2006). In its photo-induced excited state, 8HQ converts to

zwitterionic isomers, in which the hydrogen atom is transferred from oxygen to nitrogen (Bardez *et al.*, 1997). The complexes as well as the heterocycle itself exhibit antiseptic, disinfectant, and pesticidal properties (Phillips *et al.*, 1956) and functions as a transcription inhibitor (Wen *et al.*, 2023). Its solution in alcohol is used in liquid bandages. It once was of interest as an anti-cancer drug (Zhu *et al.*, 2017; Fouda 2017). The roots of the invasive plant *Centaurea diffusa* release 8HQ, which has a negative effect on plants that have not co-evolved with it (Vivanco *et al.*, 2004).

1,5-Naphthalenedisulfonic acid (H₂NDS, Armstrong acid, C₁₀H₈O₆S₂) is a white-to-yellowish solid that is soluble in water (1030 g l⁻¹). It is used in the production of dyes, pigments, and other industrial chemicals. It also functions as a chelating and complexing agent, which is used in various applications such as water treatment, analytical chemistry, and mineral processing (Arslan-Alaton *et al.*, 2008). H₂NDS does not demonstrate a definite biological activity. Complexes derived from H₂NDS are of interest in supramolecular chemistry due to their ability to form complex hydrogen-bonded systems because the sulfonate group can accept up to six hydrogen bonds.

Preparation and structural characterization of organic salts on basis of these two simple compounds is of interest for supramolecular and analytical chemistry (Oh *et al.*, 2020; Chen *et al.*, 2022). In our previous works (Suyunov *et al.*, 2023a,b,c), we reported on H₂NDS and its salts involving nickel(II) and cadmium(II). In the current work, we report on preparation and molecular and crystal structures of a proton-transfer salt, 2(8HQ)⁺·NDS²⁻·4H₂O.

The asymmetric unit of the title compound consists of one 8HQ⁺ cation, half of an NDS²⁻ anion, and two water molecules of crystallization, resulting in a supramolecular associate with a 2:1:4 cation-anion-water composition. The sulfonic acid (SO₃H) groups of H₂NDS are deprotonated, with the hydrogen atoms transferred to the nitrogen atom of an 8HQ⁺ cation, and the NDS²⁻ dianion exhibits inversion symmetry, with the inversion center located at the midpoint of the C11–C11ⁱ [symmetry code: (i) $-x, 1 - y, 1 - z$] bond in the naphthalene ring system (Fig. 1). A similar salt with composition 2C₉H₈NO⁺·C₁₀H₆O₆S₂²⁻·2H₂O was previously reported (Jin *et al.*, 2014), the main difference being the presence of

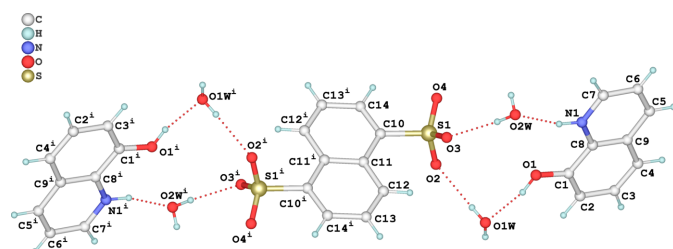


Figure 1

The structures of the molecular entities in the title salt, showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius and hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, 1 - y, 1 - z$.]

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the C10/ C11/C11'–C13'/C14 and C11–C13/ C14'/C10'/C11' rings, respectively, where primed atoms are related by the symmetry operation $-x, 1 - y, 1 - z$.

D–H...A	D–H	H...A	D...A	D–H...A
O2W–H2WA...O2 ⁱ	0.85	1.98	2.8239 (16)	176
O2W–H2WB...O3	0.85	2.02	2.8610 (15)	168
O1W–H1WA...O2	0.85	1.98	2.8150 (17)	169
O1W–H1WB...O4 ⁱⁱ	0.85	2.05	2.8806 (18)	166
O1–H1...O1W	0.82 (1)	1.84 (1)	2.6390 (16)	165 (2)
N1–H1A...O2W	0.87 (1)	1.89 (1)	2.7347 (18)	164 (2)
C6–H6...O3 ⁱⁱⁱ	0.93	2.46	3.3153 (19)	154
C4–H4...O4 ^{iv}	0.93	2.45	3.352 (2)	165
C14–H14...O1 ^v	0.93	2.57	3.3173 (18)	137
C12–H12...O3	0.93	2.46	3.0439 (17)	121
C7–H7...Cg1 ⁱ	0.93	2.82	3.6125 (17)	144
C7–H7...Cg2 ⁱⁱⁱ	0.93	2.82	3.6125 (17)	144

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $-x + 1, -y + 1, -z$; (v) $x - 1, y, z$.

only two water molecules and orthorhombic symmetry (space group *Pbca*) compared to four water molecules and monoclinic symmetry (space group *P2₁/n*) for the title salt. In the cation of the title salt, the angle around the protonated N atom [C7–N1–C8 = 122.67 (13)°] is approximately 1° less than the corresponding angle in the study of the dihydrate [123.5 (3)°]. In the title salt, the anions exhibit two distinct orientations, with the angle between their planes being 33.37 (7)°. The cations are oriented in a single direction, forming angles of 71.66 (8) and 75.80 (9)° with the planes of the anions. The naphthalene ring system exhibits typical bond lengths and angles, with C–C bond lengths ranging from 1.362 (2) to 1.431 (2) Å, and C–C–C angles in the range 117.91 (14) to 123.05 (12)°. The hydroxyquinoline and naphthalene fragments are coplanar with r.m.s deviations of 0.0162 (14) Å and 0.0112 (13) Å.

In the crystal, the 8HQ⁺ cation, the NDS²⁻ anion, and the water molecules are connected *via* classical O–H...O and N–H...O hydrogen bonds (Table 1) with graph-set motifs of R₄³(10) and R₄⁴(13), which link the components into chains extending parallel to [010], as illustrated in Fig. 2. The SO₃⁻

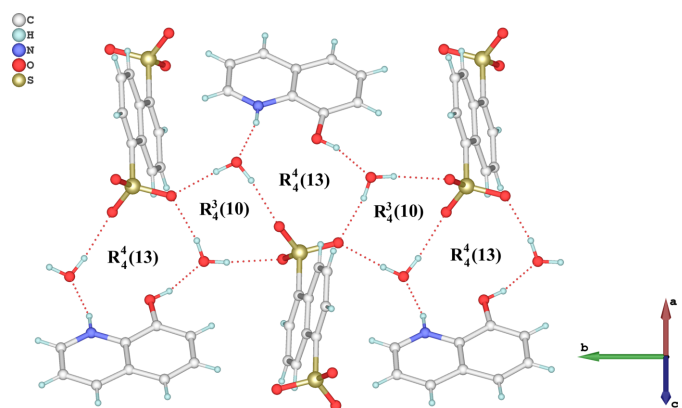


Figure 2

The formation of O–H...O and N–H...O hydrogen bonds (dashed red lines) in the crystal structure, leading to R₄³(10) and R₄⁴(13) graph-set motifs.

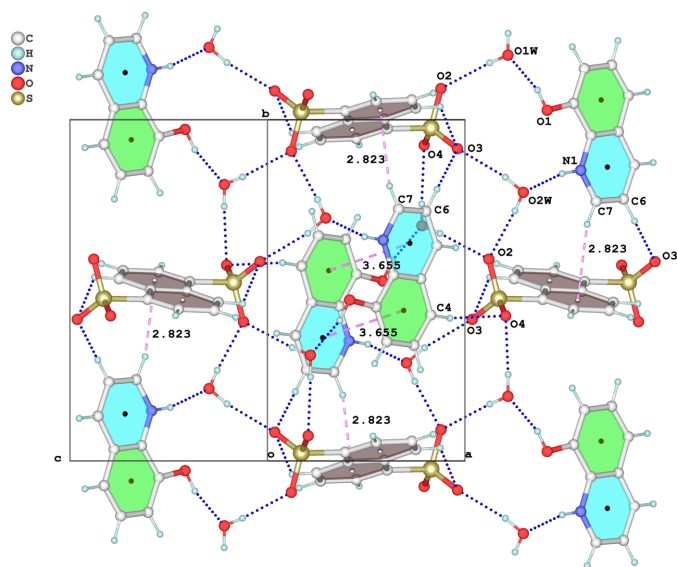


Figure 3

The crystal packing of the title salt in a view along $[10\bar{1}]$. O—H...O, N—H...O, and C—H...O hydrogen bonds are shown as dashed blue lines, and C—H... π and π — π interactions as dashed pink lines.

group on one side of the anion participates in the formation of these chains. The symmetry-related second SO_3^- group also participates in hydrogen bonding under the formation of a second infinite chain parallel to $[10\bar{1}]$ connecting with the previous chains *via* C—H... π interactions (where C_g are the centroids of the naphthalene rings, Table 1) and C(π)...C, N(π) weak intermolecular contacts [C_g ... C_g distance = 3.6547 (9) Å, slippage 1.248 Å], forming sheets parallel to (101) (Fig. 3). These sheets are linked through additional weak C—H...O interactions into a tri-periodic network structure. Due to steric hindrance of the sulfonate groups, the nearest centroid separation between naphthalene rings is 5.264 (3) Å, suggesting no π — π stacking between these moieties.

A search of the Cambridge Structural Database (CSD, version 5.45, updated November 2023; Groom *et al.*, 2016) revealed that the crystal structure of 8HQ alone has been determined eleven times, while thirteen reports are related to molecular complexes, and 71 crystals are organic salts where the nitrogen atom of 8HQ is protonated. In the case of 1,5-NDSA, 225 crystals are organic salts of 1,5-NDSA in the dianionic form, One compound (FIVFOI01; Du *et al.*, 2019) is a complex with 1,5-NDSA in the monoanionic form, and four crystals are molecular complexes (SAHRIG, Singh *et al.*, 2021; SATBEX, Liu *et al.*, 2017; VEGHUN, Cunha *et al.*, 2017; WEZGAN, Xu *et al.*, 2023) with neutral sulfo-acid molecules.

Synthesis and crystallization

The title compound was obtained by the addition of 1,5-naphthalenedisulfonate acid (0.288 g, 1 mmol) to a solution of 8-hydroxyquinoline (0.176 g, 2 mmol) in water, in the stoichiometric ratio 1:2. Good-quality single crystals were obtained by slow evaporation after four days (yield: 60%).

Table 2

Experimental details.

Crystal data	$2\text{C}_9\text{H}_8\text{NO}^+\cdot\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-}\cdot 4\text{H}_2\text{O}$
Chemical formula	650.66
M_r	Monoclinic, $P2_1/n$
Crystal system, space group	290
Temperature (K)	7.55855 (8), 12.16674 (13), 16.00467 (17)
a, b, c (Å)	β (°) 94.7152 (10)
V (Å ³)	1466.86 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.25
Crystal size (mm)	0.32 × 0.3 × 0.28
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Multi-scan (CrysAlis PRO; Rigaku OD, 2022)
T_{\min}, T_{\max}	0.820, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14094, 2841, 2621
R_{int}	0.026
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.615
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.089, 1.05
No. of reflections	2841
No. of parameters	214
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.20, -0.30

Computer programs: CrysAlis PRO (Rigaku OD, 2022), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009) and publCIF (Westrip, 2010).

Refinement

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

Funding information

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full crystallographic data

IUCrData (2024). **9**, x240570 [https://doi.org/10.1107/S2414314624005704]

Bis(8-hydroxyquinolinium) naphthalene-1,5-disulfonate tetrahydrate

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Bis(8-hydroxyquinolinium) naphthalene-1,5-disulfonate tetrahydrate

Crystal data

$2\text{C}_9\text{H}_8\text{NO}^+\cdot\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-}\cdot 4\text{H}_2\text{O}$

$M_r = 650.66$

Monoclinic, $P2_1/n$

$a = 7.55855$ (8) Å

$b = 12.16674$ (13) Å

$c = 16.00467$ (17) Å

$\beta = 94.7152$ (10)°

$V = 1466.86$ (3) Å³

$Z = 2$

$F(000) = 680$

$D_x = 1.473$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 9285 reflections

$\theta = 2.8\text{--}71.2^\circ$

$\mu = 2.25$ mm⁻¹

$T = 290$ K

Block, light yellow

$0.32 \times 0.3 \times 0.28$ mm

Data collection

XtaLAB Synergy, Single source at home/near,

HyPix3000

diffractometer

Radiation source: micro-focus sealed X-ray

tube, PhotonJet (Cu) X-ray Source

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2022)

$T_{\min} = 0.820$, $T_{\max} = 1.000$

14094 measured reflections

2841 independent reflections

2621 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 71.4^\circ$, $\theta_{\min} = 4.6^\circ$

$h = -9 \rightarrow 9$

$k = -14 \rightarrow 14$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.089$

$S = 1.05$

2841 reflections

214 parameters

2 restraints

Primary atom site location: intrinsic phasing

Secondary atom site location: difference Fourier

map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.303P]$

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

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

$\Delta\rho_{\max} = 0.20$ e Å⁻³

$\Delta\rho_{\min} = -0.29$ e Å⁻³

Extinction correction: SHELXL-2019/2

(Sheldrick 2015b),

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

Extinction coefficient: 0.0023 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atoms attached to the N and O atoms were located from a difference-Fourier map and refined with bond-length restraints of 0.86 (1) Å and 0.82 (1) Å, respectively.

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.12659 (4)	0.52366 (3)	0.29817 (2)	0.03571 (13)
O2	0.16257 (16)	0.40840 (9)	0.28388 (7)	0.0539 (3)
O3	0.28637 (14)	0.58461 (9)	0.32385 (6)	0.0451 (3)
O4	0.02239 (15)	0.57423 (10)	0.22875 (6)	0.0525 (3)
C10	−0.00953 (17)	0.52607 (10)	0.38419 (8)	0.0315 (3)
C11	0.05915 (16)	0.49755 (10)	0.46738 (8)	0.0297 (3)
C12	0.23846 (17)	0.46556 (11)	0.48773 (9)	0.0351 (3)
H12	0.315658	0.460895	0.445520	0.042*
C13	0.29860 (18)	0.44165 (13)	0.56821 (9)	0.0407 (3)
H13	0.417007	0.422577	0.580589	0.049*
C14	−0.18313 (18)	0.55446 (12)	0.36709 (9)	0.0379 (3)
H14	−0.225612	0.571361	0.312413	0.045*
O1	0.60496 (18)	0.47210 (9)	0.18830 (7)	0.0538 (3)
N1	0.68475 (17)	0.64774 (10)	0.09816 (8)	0.0415 (3)
C1	0.6624 (2)	0.45179 (12)	0.11258 (9)	0.0409 (3)
C2	0.6827 (2)	0.35003 (13)	0.07829 (10)	0.0500 (4)
H2	0.659051	0.287453	0.108831	0.060*
C3	0.7392 (2)	0.33952 (15)	−0.00293 (11)	0.0563 (4)
H3	0.750754	0.269640	−0.025395	0.068*
C4	0.7774 (2)	0.42843 (15)	−0.04946 (10)	0.0538 (4)
H4	0.814252	0.419332	−0.103052	0.065*
C5	0.7981 (2)	0.63185 (15)	−0.05880 (10)	0.0520 (4)
H5	0.836512	0.627362	−0.112434	0.062*
C6	0.7791 (2)	0.73209 (15)	−0.02321 (11)	0.0550 (4)
H6	0.804189	0.795738	−0.052154	0.066*
C7	0.7214 (2)	0.73849 (13)	0.05723 (11)	0.0500 (4)
H7	0.708614	0.806722	0.082224	0.060*
C8	0.70289 (18)	0.54549 (12)	0.06544 (9)	0.0370 (3)
C9	0.7607 (2)	0.53461 (13)	−0.01585 (9)	0.0426 (3)
O1W	0.49949 (17)	0.31023 (10)	0.28209 (9)	0.0626 (3)
H1WA	0.392446	0.331508	0.282471	0.094*
H1WB	0.491769	0.242369	0.269682	0.094*
O2W	0.53570 (16)	0.71260 (10)	0.24017 (8)	0.0556 (3)
H2WA	0.480634	0.773241	0.233271	0.083*
H2WB	0.460317	0.669091	0.258790	0.083*
H1A	0.643 (3)	0.6562 (18)	0.1467 (8)	0.069 (6)*
H1	0.581 (3)	0.4147 (13)	0.2114 (14)	0.086 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0424 (2)	0.0381 (2)	0.02794 (19)	-0.00473 (12)	0.01084 (14)	-0.00284 (12)
O2	0.0634 (7)	0.0416 (6)	0.0599 (7)	-0.0036 (5)	0.0242 (6)	-0.0135 (5)
O3	0.0471 (6)	0.0540 (6)	0.0360 (5)	-0.0140 (5)	0.0142 (4)	-0.0021 (4)
O4	0.0584 (7)	0.0706 (8)	0.0291 (5)	-0.0020 (5)	0.0078 (5)	0.0066 (5)
C10	0.0356 (7)	0.0308 (6)	0.0289 (6)	-0.0024 (5)	0.0074 (5)	0.0001 (5)
C11	0.0312 (6)	0.0285 (6)	0.0300 (6)	-0.0018 (5)	0.0066 (5)	0.0002 (5)
C12	0.0317 (7)	0.0393 (7)	0.0356 (7)	0.0018 (5)	0.0102 (5)	0.0026 (5)
C13	0.0307 (7)	0.0489 (8)	0.0428 (8)	0.0052 (6)	0.0047 (6)	0.0054 (6)
C14	0.0385 (7)	0.0442 (8)	0.0309 (7)	0.0004 (6)	0.0021 (5)	0.0043 (5)
O1	0.0785 (8)	0.0460 (7)	0.0388 (6)	-0.0095 (6)	0.0159 (6)	0.0057 (5)
N1	0.0483 (7)	0.0403 (6)	0.0360 (6)	-0.0024 (5)	0.0041 (5)	0.0042 (5)
C1	0.0443 (8)	0.0437 (8)	0.0345 (7)	-0.0027 (6)	0.0017 (6)	0.0049 (6)
C2	0.0571 (9)	0.0407 (8)	0.0518 (9)	-0.0019 (7)	0.0026 (7)	0.0059 (7)
C3	0.0661 (10)	0.0474 (9)	0.0555 (10)	0.0066 (8)	0.0056 (8)	-0.0076 (7)
C4	0.0599 (10)	0.0613 (10)	0.0409 (8)	0.0071 (8)	0.0092 (7)	-0.0043 (7)
C5	0.0525 (9)	0.0649 (11)	0.0398 (8)	0.0007 (7)	0.0104 (7)	0.0136 (7)
C6	0.0582 (10)	0.0532 (10)	0.0543 (10)	-0.0050 (8)	0.0090 (8)	0.0210 (8)
C7	0.0570 (9)	0.0396 (8)	0.0532 (9)	-0.0028 (7)	0.0033 (7)	0.0076 (7)
C8	0.0370 (7)	0.0413 (7)	0.0321 (7)	-0.0018 (5)	0.0000 (5)	0.0029 (5)
C9	0.0400 (7)	0.0533 (9)	0.0344 (7)	0.0013 (6)	0.0033 (6)	0.0046 (6)
O1W	0.0647 (8)	0.0529 (7)	0.0722 (8)	0.0003 (6)	0.0171 (7)	0.0131 (6)
O2W	0.0629 (7)	0.0451 (6)	0.0618 (7)	0.0057 (5)	0.0236 (6)	0.0069 (5)

Geometric parameters (\AA , $^\circ$)

S1—O2	1.4503 (11)	C1—C8	1.414 (2)
S1—O3	1.4476 (10)	C2—H2	0.9300
S1—O4	1.4455 (11)	C2—C3	1.407 (2)
S1—C10	1.7853 (13)	C3—H3	0.9300
C10—C11	1.4314 (18)	C3—C4	1.358 (3)
C10—C14	1.3627 (19)	C4—H4	0.9300
C11—C11 ⁱ	1.431 (2)	C4—C9	1.409 (2)
C11—C12	1.4219 (18)	C5—H5	0.9300
C12—H12	0.9300	C5—C6	1.359 (3)
C12—C13	1.362 (2)	C5—C9	1.409 (2)
C13—H13	0.9300	C6—H6	0.9300
C13—C14 ⁱ	1.409 (2)	C6—C7	1.395 (2)
C14—H14	0.9300	C7—H7	0.9300
O1—C1	1.3433 (19)	C8—C9	1.412 (2)
O1—H1	0.819 (10)	O1W—H1WA	0.8500
N1—C7	1.3246 (19)	O1W—H1WB	0.8501
N1—C8	1.3611 (19)	O2W—H2WA	0.8498
N1—H1A	0.868 (9)	O2W—H2WB	0.8495
C1—C2	1.368 (2)		

O2—S1—C10	105.37 (6)	C2—C1—C8	118.63 (14)
O3—S1—O2	112.16 (7)	C1—C2—H2	119.8
O3—S1—C10	107.03 (6)	C1—C2—C3	120.36 (15)
O4—S1—O2	112.81 (7)	C3—C2—H2	119.8
O4—S1—O3	112.91 (7)	C2—C3—H3	119.0
O4—S1—C10	105.88 (6)	C4—C3—C2	121.91 (16)
C11—C10—S1	121.69 (10)	C4—C3—H3	119.0
C14—C10—S1	117.11 (10)	C3—C4—H4	120.3
C14—C10—C11	121.19 (12)	C3—C4—C9	119.43 (15)
C11 ⁱ —C11—C10	117.91 (14)	C9—C4—H4	120.3
C12—C11—C10	123.05 (12)	C6—C5—H5	119.4
C12—C11—C11 ⁱ	119.03 (14)	C6—C5—C9	121.12 (15)
C11—C12—H12	119.6	C9—C5—H5	119.4
C13—C12—C11	120.86 (12)	C5—C6—H6	120.4
C13—C12—H12	119.6	C5—C6—C7	119.28 (15)
C12—C13—H13	119.7	C7—C6—H6	120.4
C12—C13—C14 ⁱ	120.62 (13)	N1—C7—C6	120.25 (15)
C14 ⁱ —C13—H13	119.7	N1—C7—H7	119.9
C10—C14—C13 ⁱ	120.36 (13)	C6—C7—H7	119.9
C10—C14—H14	119.8	N1—C8—C1	119.89 (13)
C13 ⁱ —C14—H14	119.8	N1—C8—C9	119.25 (13)
C1—O1—H1	110.6 (17)	C9—C8—C1	120.85 (14)
C7—N1—C8	122.67 (13)	C4—C9—C8	118.80 (14)
C7—N1—H1A	116.7 (15)	C5—C9—C4	123.77 (15)
C8—N1—H1A	120.6 (15)	C5—C9—C8	117.43 (14)
O1—C1—C2	125.70 (14)	H1WA—O1W—H1WB	104.5
O1—C1—C8	115.67 (13)	H2WA—O2W—H2WB	104.5
S1—C10—C11—C11 ⁱ	179.61 (12)	N1—C8—C9—C4	-179.40 (14)
S1—C10—C11—C12	0.00 (18)	N1—C8—C9—C5	0.5 (2)
S1—C10—C14—C13 ⁱ	-179.89 (11)	C1—C2—C3—C4	0.8 (3)
O2—S1—C10—C11	69.66 (12)	C1—C8—C9—C4	0.0 (2)
O2—S1—C10—C14	-109.23 (12)	C1—C8—C9—C5	179.91 (14)
O3—S1—C10—C11	-49.90 (12)	C2—C1—C8—N1	-179.68 (14)
O3—S1—C10—C14	131.21 (11)	C2—C1—C8—C9	0.9 (2)
O4—S1—C10—C11	-170.60 (10)	C2—C3—C4—C9	0.1 (3)
O4—S1—C10—C14	10.52 (13)	C3—C4—C9—C5	179.58 (16)
C10—C11—C12—C13	178.45 (13)	C3—C4—C9—C8	-0.5 (2)
C11—C10—C14—C13 ⁱ	1.2 (2)	C5—C6—C7—N1	-0.4 (3)
C11 ⁱ —C11—C12—C13	-1.1 (2)	C6—C5—C9—C4	179.83 (16)
C11—C12—C13—C14 ⁱ	1.5 (2)	C6—C5—C9—C8	0.0 (2)
C14—C10—C11—C11 ⁱ	-1.6 (2)	C7—N1—C8—C1	179.67 (14)
C14—C10—C11—C12	178.84 (13)	C7—N1—C8—C9	-0.9 (2)
O1—C1—C2—C3	178.11 (15)	C8—N1—C7—C6	0.8 (2)
O1—C1—C8—N1	0.9 (2)	C8—C1—C2—C3	-1.3 (2)
O1—C1—C8—C9	-178.57 (13)	C9—C5—C6—C7	0.0 (3)

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

Hydrogen-bond geometry (Å, °)

*Cg*1 and *Cg*2 are the centroids of the C10/ C11/C11'-C13'/C14 and C11-C13/C14/C10'/C11' rings, respectively, where primed atoms are related by the symmetry operation $-x, 1-y, 1-z$.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2 <i>W</i> —H2 <i>WA</i> ···O2 ⁱⁱ	0.85	1.98	2.8239 (16)	176
O2 <i>W</i> —H2 <i>WB</i> ···O3	0.85	2.02	2.8610 (15)	168
O1 <i>W</i> —H1 <i>WA</i> ···O2	0.85	1.98	2.8150 (17)	169
O1 <i>W</i> —H1 <i>WB</i> ···O4 ⁱⁱⁱ	0.85	2.05	2.8806 (18)	166
O1—H1···O1 <i>W</i>	0.82 (1)	1.84 (1)	2.6390 (16)	165 (2)
N1—H1 <i>A</i> ···O2 <i>W</i>	0.87 (1)	1.89 (1)	2.7347 (18)	164 (2)
C6—H6···O3 ^{iv}	0.93	2.46	3.3153 (19)	154
C4—H4···O4 ^v	0.93	2.45	3.352 (2)	165
C14—H14···O1 ^{vi}	0.93	2.57	3.3173 (18)	137
C12—H12···O3	0.93	2.46	3.0439 (17)	121
C7—H7··· <i>Cg</i> 1 ⁱⁱ	0.93	2.82	3.6125 (17)	144
C7—H7··· <i>Cg</i> 2 ^{iv}	0.93	2.82	3.6125 (17)	144

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