2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)-ethenyl]-1-methylpyridinium 4-bromo-benzenesulfonate monohydrate

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The title salt crystallized as the monohydrate $C_{15}H_{16}NO_2^+$·$C_6H_4BrSO_3^-$·H_2O. The cation exists in an *E* conformation with respect to the ethynyl bond and is essentially planar, with a dihedral angle of 6.52 (14)° between the pyridinium and the benzene rings. The hydroxy and methoxy substituents are coplanar with the benzene ring to which they are attached, with an r.m.s. deviation of 0.0116 (3) Å for the nine non-H atoms [C_{methyl}—O—C—C torsion angle = −0.8 (4)°]. In the crystal, the cations and anions are stacked by π–π interactions, with centroid–centroid distances of 3.7818 (19) and 3.9004 (17) Å. The cations, anions and water molecules are linked by O—H···O hydrogen bonds and weak C—H···O interactions, forming a three-dimensional network.

Related literature

For applications of stilbene derivatives, see: Chanawanno *et al.* (2010); Frombaum *et al.* (2012); Hussain *et al.* (2009); Jindawong *et al.* (2005); Kobkeatthawin *et al.* (2009); Li *et al.* (2013); Ruanwas *et al.* (2010). For related structures, see, Chanawanno *et al.* (2009); Chantrapromma *et al.* (2013); Fun *et al.* (2011). For bond-length data, see: Allen *et al.* (1987) and for hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer, (1986).

Experimental

Crystal data

$C_{15}H_{16}NO_2^+$·$C_6H_4BrO_3S^-$·H_2O	γ = 107.042 (2)°
M_r = 496.37	V = 1074.1 (3) Å³
Triclinic, $P\bar{1}$	Z = 2
a = 9.8201 (13) Å	Mo $K\alpha$ radiation
b = 10.3315 (14) Å	μ = 2.05 mm⁻¹
c = 12.4914 (17) Å	T = 100 K
α = 99.898 (2)°	0.59 × 0.15 × 0.14 mm
β = 111.134 (2)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	11172 measured reflections
	4186 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	3356 reflections with $I > 2\sigma(I)$
T_{min} = 0.378, T_{max} = 0.768	R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.113	
S = 1.05	
4186 reflections	$\Delta\rho_{max}$ = 0.93 e Å⁻³
281 parameters	$\Delta\rho_{min}$ = −0.94 e Å⁻³

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1O2···O1W^i	0.82	1.88	2.685 (4)	169
O1W—H2W1···O4^{ii}	0.81 (5)	2.03 (5)	2.834 (4)	172 (5)
O1W—H1W1···O3^{iii}	0.81 (4)	1.99 (5)	2.793 (5)	173 (5)
C1—H1A···O5^{iv}	0.93	2.57	3.491 (4)	170
C2—H2A···O1^v	0.93	2.51	3.440 (4)	176
C2—H2A···O2^v	0.93	2.60	3.183 (4)	121
C3—H3A···O2^v	0.93	2.54	3.160 (4)	124
C14—H14A···O4^{iv}	0.96	2.54	3.448 (5)	158

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

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organic compounds

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ5370).

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2-[(*E*)-2-(4-Hydroxy-3-methoxyphenyl)ethenyl]-1-methylpyridinium 4-bromo-benzenesulfonate monohydrate

Suchada Chantrapromma, Nawong Boonnak, Boonwasana Jindawong and Hoong-Kun Fun

1. Comment

Stilbene-based compounds have been reported to possess a wide range of biological activities including antibacterial (Chanawanno *et al.*, 2010) and antioxidant (Frombaum *et al.*, 2012) activities and also non-linear optical (Ruanwas *et al.*, 2010) and fluorescent properties (Li *et al.*, 2013). We have previously reported several crystal structures and applications of stilbene derivatives (Chanawanno *et al.*, 2009; 2010, Kobkeatthawin *et al.*, 2009, Ruanwas *et al.*, 2010). Due to these interesting properties, the title pyridinium-stilbene salt, (I), was synthesized. We report herein the synthesis and crystal structure of (I).

The asymmetric unit of (I) consists of a $C_{15}H_{16}NO_2^+$ cation, a $C_6H_4BrSO_3^-$ anion and an H_2O molecule (Fig. 1). The cation exists in an *E* configuration with respect to the C6＝C7 double bond [1.318 (4) Å] and the C5—C6—C7—C8 torsion angle is -178.0 (3)°. The cation is essentially planar with a dihedral angle between the pyridinium and benzene rings of the cation being 6.52 (14)°. The hydroxy and methoxy substituents lie close to the plane of the C8–C13 benzene ring with the *r.m.s.* deviation of 0.0116 (3) Å for the nine non-H atoms and with the torsion angle C15–O1–C10–C9 = -0.8 (4)°. All bond lengths (Allen *et al.*, 1987) in both the cation and anion are normal and compare well with those found in closely related structures (Chanawanno *et al.*, 2009; Chantrapromma *et al.*, 2013; Fun *et al.*, 2011).

In the crystal packing (Fig. 2), weak C2—H2A···O1 and C3—H3A···O2 interactions (Table 1) link together two inversely-related adjacent cations, generating an $R_2^2(8)$ ring motif (Bernstein *et al.*, 1995). The O1W—H1W1···O3 and O1W—H2W1···O4 hydrogen bonds (Table 1) linked between two water molecules and two anions forming an $R_2^4(12)$ ring motif. The cations, anions and water molecules are further linked through intermolecular O–H···O hydrogen bonds and weak C—H···O interactions into a three dimensional network (Fig. 2 and Table 1). π–π interactions with distances $Cg_1···Cg_3^{vi}$ = 3.7818 (19) Å and $Cg_2···Cg_3^{ii}$ = 3.9004 (17) Å were observed (Fig. 3); Cg_1, Cg_2 and Cg_3 are the centroids of C1–C5/N1, C8–C13 and C16–C21 rings, respectively [symmetry code (vi) = 1 - *x*, 1 - *y*, 1 - *z*].

2. Experimental

1-Methyl-2-[(*E*)-2-(3-methoxy-4-hydroxyphenyl)ethenyl]pyridinium iodide (compound A) was prepared by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylpyridinium iodide (3.02 g, 12.84 mmol), vanillin (4-hydroxy-3-methoxy-benzaldehyde, 1.95 g, 12.82 mmol) and piperidine (1.09 g, 12.80 mmol). The resulting solution was refluxed for 3 h under a nitrogen atmosphere. The solid which formed was filtered, washed with diethylether and recrystallized from methanol, to give brown crystals of compound A (2.69 g, 57% yield Mp. 526–527 K). Thereafter, the title compound was synthesized by mixing a solution of compound A (0.21 g, 0.58 mmol) in hot methanol (60 ml) and a solution of silver (I) 4-bromobenzenesulfonate (Jindawong *et al.*, 2005), (0.20 g, 0.58 mmol) in hot methanol (40 ml). Upon mixing, a yellow precipitate of silver iodide was immediately formed which was removed by filtration and the orange filtrate was evaporated under reduced pressure to yield the title compound as an orange solid (0.27 g, 91% yield). Orange block-

shaped single crystals of the title compound suitable for X-ray structure determination were recrystallized from methanol by slow evaporation of the solvent at room temperature over several days, Mp. 490–491 K.

3. Refinement

Water H atoms were located in difference maps and refined isotropically. The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(O—H) = 0.82 Å, d(C—H) = 0.93 Å for aromatic and CH, and 0.96 Å for CH$_3$ atoms. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the methyl groups.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).
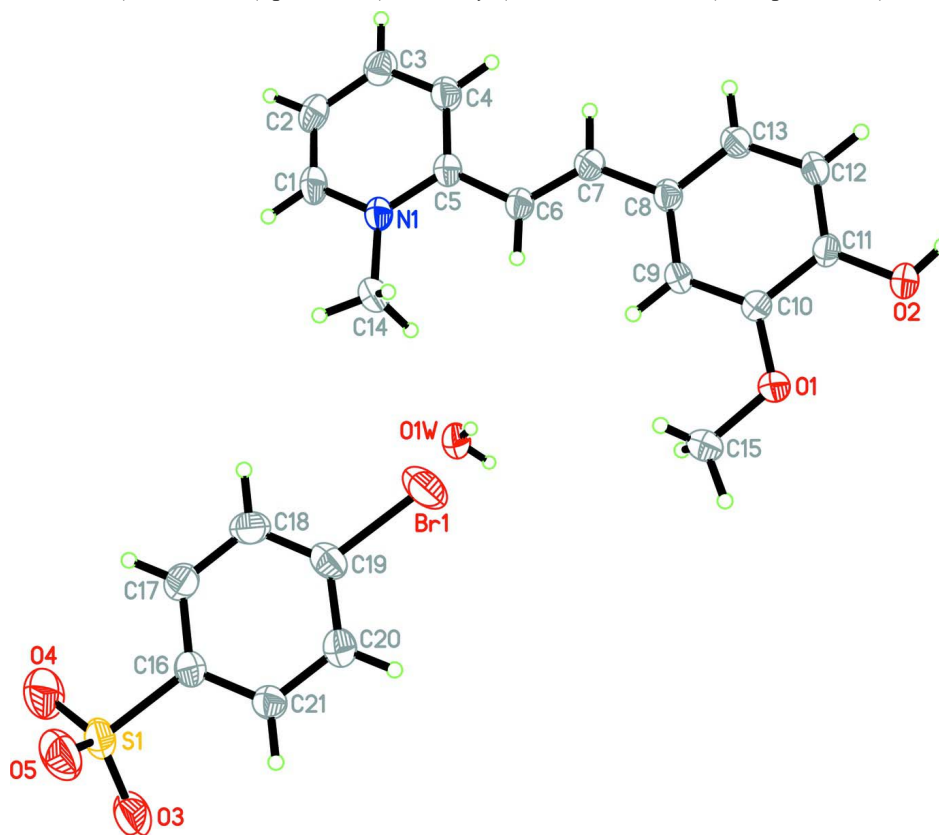

Figure 1

The molecular structure of the title compound, showing 30% probability displacement ellipsoids.
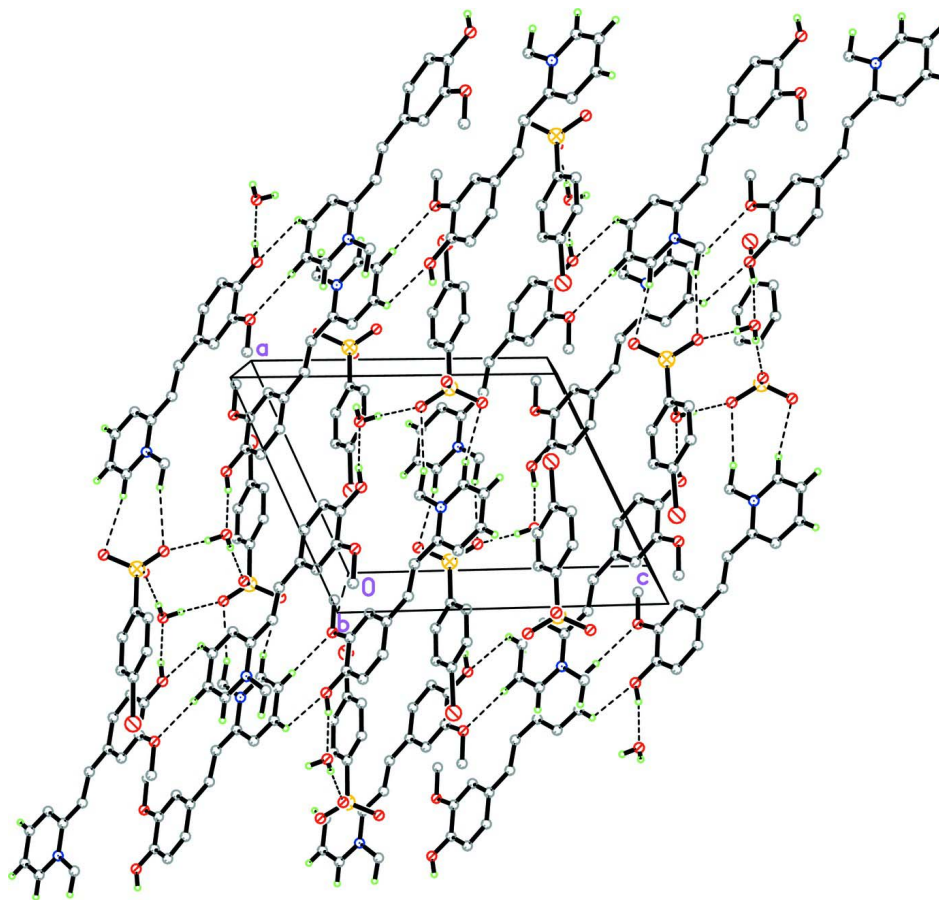
Figure 2

The crystal packing of the title compound viewed approximately along the *b* axis. Only H atoms involved in O—H⋯O hydrogen bonds and weak C—H⋯O interactions are shown for clarity. Hydrogen bonds are drawn as dashed lines.
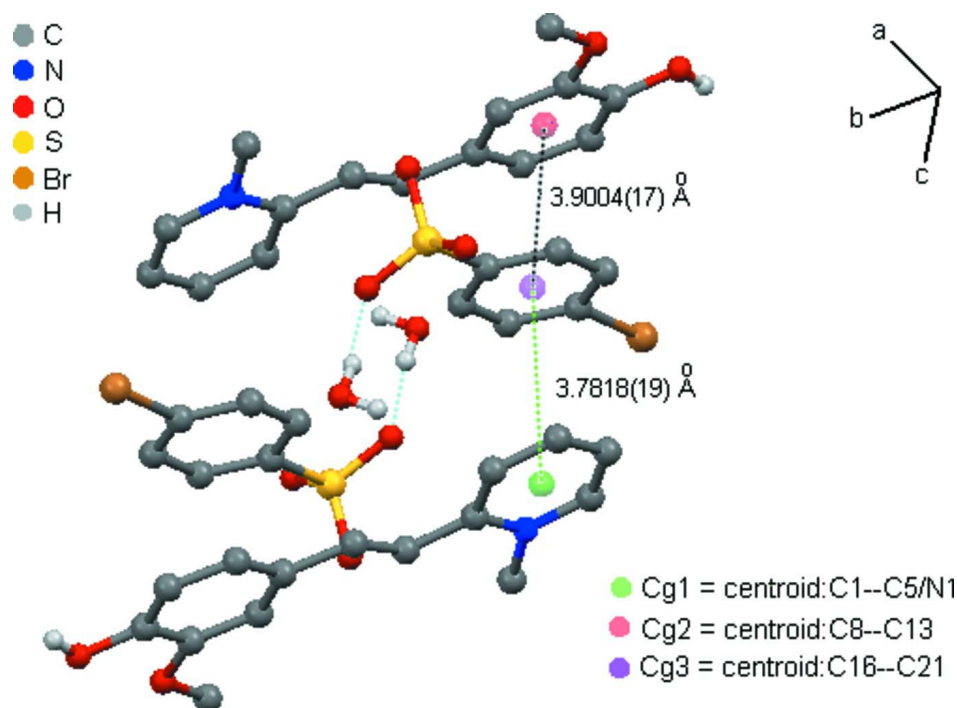
Figure 3

π–π interactions between aromatic rings of the cations and anions.

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Crystal data

$C_{15}H_{16}NO_2{}^+ \cdot C_6H_4BrO_3S^- \cdot H_2O$	$Z = 2$
$M_r = 496.37$	$F(000) = 508$
Triclinic, $P\bar{1}$	$D_x = 1.535$ Mg m^{-3}
Hall symbol: -P 1	Melting point = 490–491 K
$a = 9.8201$ (13) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 10.3315$ (14) Å	Cell parameters from 4186 reflections
$c = 12.4914$ (17) Å	$\theta = 1.8$–26.0°
$\alpha = 99.898$ (2)°	$\mu = 2.05$ mm^{-1}
$\beta = 111.134$ (2)°	$T = 100$ K
$\gamma = 107.042$ (2)°	Block, orange
$V = 1074.1$ (3) Å^3	0.59 × 0.15 × 0.14 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	11172 measured reflections
Radiation source: sealed tube	4186 independent reflections
Graphite monochromator	3356 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$\theta_{max} = 26.0°$, $\theta_{min} = 1.8°$
	$h = -12 \rightarrow 12$
	$k = -12 \rightarrow 12$
$T_{min} = 0.378$, $T_{max} = 0.768$	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.113$	
$S = 1.05$	H atoms treated by a mixture of independent and constrained refinement
4186 reflections	
281 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.8763P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.001$
	$\Delta\rho_{max} = 0.93$ e Å^{-3}
	$\Delta\rho_{min} = -0.94$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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

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_{iso}*/U_{eq}
Br1	0.41562 (5)	0.27735 (5)	0.15160 (5)	0.0940 (2)
S1	1.07185 (8)	0.19371 (9)	0.35750 (8)	0.0644 (2)
O1	−0.2430 (2)	0.1320 (2)	−0.12616 (19)	0.0664 (6)
O2	−0.4997 (2)	0.1780 (2)	−0.22714 (18)	0.0617 (5)
H1O2	−0.5807	0.1942	−0.2456	0.092*
O3	1.0331 (3)	0.0475 (3)	0.3536 (3)	0.1036 (10)
O4	1.1634 (3)	0.2910 (3)	0.4784 (2)	0.1020 (9)
O5	1.1441 (3)	0.2289 (3)	0.2791 (3)	0.0922 (8)
N1	0.3889 (2)	0.6912 (2)	0.43554 (19)	0.0449 (5)
C1	0.4991 (3)	0.7901 (3)	0.5431 (2)	0.0542 (7)
H1A	0.5957	0.7823	0.5812	0.065*
C2	0.4719 (4)	0.8995 (3)	0.5961 (3)	0.0566 (7)
H2A	0.5483	0.9660	0.6698	0.068*
C3	0.3287 (4)	0.9101 (3)	0.5387 (3)	0.0586 (7)
H3A	0.3080	0.9848	0.5732	0.070*
C4	0.2177 (3)	0.8115 (3)	0.4318 (3)	0.0555 (7)
H4A	0.1215	0.8199	0.3936	0.067*
C5	0.2451 (3)	0.6974 (3)	0.3778 (2)	0.0455 (6)
C6	0.1282 (3)	0.5869 (3)	0.2659 (2)	0.0478 (6)
H6A	0.1532	0.5114	0.2388	0.057*
C7	−0.0113 (3)	0.5867 (3)	0.2003 (2)	0.0492 (6)
H7A	−0.0320	0.6648	0.2281	0.059*
C8	−0.1367 (3)	0.4785 (3)	0.0895 (2)	0.0435 (6)

C9	−0.1236 (3)	0.3541 (3)	0.0378 (2)	0.0443 (6)
H9A	−0.0318	0.3384	0.0750	0.053*
C10	−0.2452 (3)	0.2549 (3)	−0.0674 (2)	0.0446 (6)
C11	−0.3846 (3)	0.2778 (3)	−0.1224 (2)	0.0446 (6)
C12	−0.3978 (3)	0.3996 (3)	−0.0715 (2)	0.0484 (6)
H12A	−0.4902	0.4148	−0.1079	0.058*
C13	−0.2746 (3)	0.4999 (3)	0.0333 (2)	0.0513 (6)
H13A	−0.2843	0.5825	0.0665	0.062*
C14	0.4288 (3)	0.5777 (3)	0.3817 (3)	0.0575 (7)
H14A	0.5370	0.5939	0.4304	0.086*
H14B	0.4148	0.5782	0.3017	0.086*
H14C	0.3607	0.4871	0.3780	0.086*
C15	−0.1033 (4)	0.1044 (4)	−0.0758 (3)	0.0733 (10)
H15A	−0.1162	0.0160	−0.1260	0.110*
H15B	−0.0847	0.0984	0.0038	0.110*
H15C	−0.0147	0.1802	−0.0712	0.110*
C16	0.8901 (3)	0.2169 (3)	0.3001 (2)	0.0474 (6)
C17	0.8818 (4)	0.3438 (3)	0.3475 (3)	0.0577 (7)
H17A	0.9713	0.4164	0.4103	0.069*
C18	0.7421 (4)	0.3636 (3)	0.3025 (3)	0.0649 (8)
H18A	0.7365	0.4492	0.3339	0.078*
C19	0.6110 (3)	0.2548 (3)	0.2102 (3)	0.0568 (7)
C20	0.6163 (3)	0.1274 (3)	0.1621 (3)	0.0547 (7)
H20A	0.5259	0.0546	0.1002	0.066*
C21	0.7575 (3)	0.1089 (3)	0.2070 (2)	0.0519 (6)
H21A	0.7633	0.0238	0.1744	0.062*
O1W	0.2172 (3)	0.1988 (3)	0.6854 (3)	0.0753 (7)
H2W1	0.196 (5)	0.217 (5)	0.622 (4)	0.093 (16)*
H1W1	0.148 (5)	0.124 (4)	0.671 (3)	0.079 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0699 (3)	0.1027 (3)	0.1419 (4)	0.0567 (2)	0.0504 (3)	0.0641 (3)
S1	0.0390 (4)	0.0670 (5)	0.0786 (6)	0.0186 (3)	0.0175 (4)	0.0237 (4)
O1	0.0524 (11)	0.0487 (11)	0.0694 (13)	0.0257 (9)	0.0008 (10)	−0.0031 (10)
O2	0.0436 (10)	0.0497 (11)	0.0594 (12)	0.0154 (9)	−0.0018 (9)	−0.0002 (9)
O3	0.0558 (14)	0.0819 (17)	0.171 (3)	0.0330 (13)	0.0319 (16)	0.0612 (19)
O4	0.0677 (16)	0.118 (2)	0.0798 (18)	0.0354 (16)	−0.0017 (14)	0.0105 (16)
O5	0.0644 (15)	0.112 (2)	0.122 (2)	0.0398 (15)	0.0553 (16)	0.0469 (18)
N1	0.0371 (11)	0.0485 (12)	0.0416 (12)	0.0127 (9)	0.0123 (9)	0.0139 (10)
C1	0.0380 (14)	0.0643 (18)	0.0439 (15)	0.0100 (13)	0.0079 (12)	0.0178 (13)
C2	0.0526 (16)	0.0527 (16)	0.0403 (15)	0.0047 (13)	0.0113 (13)	0.0048 (12)
C3	0.0587 (18)	0.0557 (17)	0.0496 (16)	0.0162 (14)	0.0207 (14)	0.0056 (13)
C4	0.0462 (15)	0.0586 (17)	0.0508 (16)	0.0210 (13)	0.0139 (13)	0.0065 (13)
C5	0.0386 (13)	0.0493 (15)	0.0412 (14)	0.0135 (11)	0.0133 (11)	0.0125 (11)
C6	0.0393 (13)	0.0471 (14)	0.0441 (14)	0.0154 (11)	0.0103 (11)	0.0042 (11)
C7	0.0467 (14)	0.0477 (15)	0.0440 (14)	0.0187 (12)	0.0133 (12)	0.0062 (12)
C8	0.0391 (13)	0.0471 (14)	0.0377 (13)	0.0163 (11)	0.0118 (11)	0.0092 (11)
C9	0.0344 (12)	0.0466 (14)	0.0454 (14)	0.0168 (11)	0.0097 (11)	0.0137 (11)

C10	0.0416 (13)	0.0389 (13)	0.0461 (14)	0.0150 (11)	0.0130 (11)	0.0107 (11)
C11	0.0362 (12)	0.0407 (13)	0.0424 (14)	0.0091 (10)	0.0075 (11)	0.0104 (11)
C12	0.0361 (13)	0.0537 (15)	0.0470 (15)	0.0202 (12)	0.0092 (11)	0.0110 (12)
C13	0.0462 (15)	0.0524 (15)	0.0478 (15)	0.0246 (12)	0.0124 (12)	0.0063 (12)
C14	0.0448 (15)	0.0613 (17)	0.0609 (18)	0.0240 (13)	0.0149 (13)	0.0182 (14)
C15	0.0608 (19)	0.0602 (19)	0.084 (2)	0.0365 (16)	0.0133 (17)	0.0043 (17)
C16	0.0414 (13)	0.0529 (15)	0.0481 (15)	0.0163 (12)	0.0204 (12)	0.0178 (12)
C17	0.0547 (17)	0.0511 (16)	0.0597 (18)	0.0130 (13)	0.0259 (15)	0.0107 (14)
C18	0.070 (2)	0.0483 (16)	0.089 (2)	0.0268 (15)	0.0453 (19)	0.0212 (16)
C19	0.0525 (16)	0.0658 (19)	0.0734 (19)	0.0317 (15)	0.0359 (15)	0.0370 (16)
C20	0.0464 (15)	0.0619 (17)	0.0501 (16)	0.0190 (13)	0.0174 (13)	0.0159 (13)
C21	0.0498 (15)	0.0536 (16)	0.0513 (16)	0.0227 (13)	0.0217 (13)	0.0098 (13)
O1W	0.0510 (14)	0.0705 (17)	0.0782 (19)	0.0190 (13)	0.0064 (12)	0.0174 (14)

Geometric parameters (Å, º)

Br1—C19	1.892 (3)	C8—C9	1.398 (4)
S1—O3	1.433 (3)	C9—C10	1.375 (4)
S1—O5	1.438 (3)	C9—H9A	0.9300
S1—O4	1.438 (3)	C10—C11	1.404 (4)
S1—C16	1.773 (3)	C11—C12	1.373 (4)
O1—C10	1.363 (3)	C12—C13	1.382 (4)
O1—C15	1.425 (3)	C12—H12A	0.9300
O2—C11	1.356 (3)	C13—H13A	0.9300
O2—H1O2	0.8200	C14—H14A	0.9600
N1—C1	1.360 (3)	C14—H14B	0.9600
N1—C5	1.361 (3)	C14—H14C	0.9600
N1—C14	1.473 (4)	C15—H15A	0.9600
C1—C2	1.355 (4)	C15—H15B	0.9600
C1—H1A	0.9300	C15—H15C	0.9600
C2—C3	1.376 (4)	C16—C21	1.380 (4)
C2—H2A	0.9300	C16—C17	1.381 (4)
C3—C4	1.357 (4)	C17—C18	1.373 (4)
C3—H3A	0.9300	C17—H17A	0.9300
C4—C5	1.400 (4)	C18—C19	1.374 (5)
C4—H4A	0.9300	C18—H18A	0.9300
C5—C6	1.449 (4)	C19—C20	1.374 (4)
C6—C7	1.318 (4)	C20—C21	1.380 (4)
C6—H6A	0.9300	C20—H20A	0.9300
C7—C8	1.454 (4)	C21—H21A	0.9300
C7—H7A	0.9300	O1W—H2W1	0.81 (4)
C8—C13	1.385 (4)	O1W—H1W1	0.80 (4)
O3—S1—O5	112.54 (19)	O2—C11—C12	122.9 (2)
O3—S1—O4	112.9 (2)	O2—C11—C10	117.3 (2)
O5—S1—O4	112.02 (19)	C12—C11—C10	119.8 (2)
O3—S1—C16	106.57 (14)	C11—C12—C13	120.4 (2)
O5—S1—C16	105.90 (14)	C11—C12—H12A	119.8
O4—S1—C16	106.35 (15)	C13—C12—H12A	119.8
C10—O1—C15	117.7 (2)	C12—C13—C8	120.6 (2)

C11—O2—H1O2	109.5	C12—C13—H13A	119.7
C1—N1—C5	121.0 (2)	C8—C13—H13A	119.7
C1—N1—C14	118.6 (2)	N1—C14—H14A	109.5
C5—N1—C14	120.4 (2)	N1—C14—H14B	109.5
C2—C1—N1	121.7 (3)	H14A—C14—H14B	109.5
C2—C1—H1A	119.1	N1—C14—H14C	109.5
N1—C1—H1A	119.1	H14A—C14—H14C	109.5
C1—C2—C3	118.6 (3)	H14B—C14—H14C	109.5
C1—C2—H2A	120.7	O1—C15—H15A	109.5
C3—C2—H2A	120.7	O1—C15—H15B	109.5
C4—C3—C2	120.1 (3)	H15A—C15—H15B	109.5
C4—C3—H3A	120.0	O1—C15—H15C	109.5
C2—C3—H3A	120.0	H15A—C15—H15C	109.5
C3—C4—C5	121.3 (3)	H15B—C15—H15C	109.5
C3—C4—H4A	119.4	C21—C16—C17	120.0 (3)
C5—C4—H4A	119.4	C21—C16—S1	120.0 (2)
N1—C5—C4	117.3 (2)	C17—C16—S1	120.0 (2)
N1—C5—C6	119.4 (2)	C18—C17—C16	120.4 (3)
C4—C5—C6	123.3 (2)	C18—C17—H17A	119.8
C7—C6—C5	124.1 (3)	C16—C17—H17A	119.8
C7—C6—H6A	118.0	C17—C18—C19	118.9 (3)
C5—C6—H6A	118.0	C17—C18—H18A	120.6
C6—C7—C8	127.6 (3)	C19—C18—H18A	120.6
C6—C7—H7A	116.2	C18—C19—C20	121.7 (3)
C8—C7—H7A	116.2	C18—C19—Br1	119.4 (2)
C13—C8—C9	118.9 (2)	C20—C19—Br1	118.8 (2)
C13—C8—C7	118.4 (2)	C19—C20—C21	119.1 (3)
C9—C8—C7	122.7 (2)	C19—C20—H20A	120.5
C10—C9—C8	120.7 (2)	C21—C20—H20A	120.5
C10—C9—H9A	119.7	C16—C21—C20	119.9 (3)
C8—C9—H9A	119.7	C16—C21—H21A	120.0
O1—C10—C9	125.3 (2)	C20—C21—H21A	120.0
O1—C10—C11	115.1 (2)	H2W1—O1W—H1W1	105 (4)
C9—C10—C11	119.6 (2)		
C5—N1—C1—C2	−1.1 (4)	O1—C10—C11—C12	−178.8 (2)
C14—N1—C1—C2	178.2 (3)	C9—C10—C11—C12	0.8 (4)
N1—C1—C2—C3	−0.2 (4)	O2—C11—C12—C13	−177.9 (3)
C1—C2—C3—C4	0.6 (5)	C10—C11—C12—C13	0.1 (4)
C2—C3—C4—C5	0.2 (5)	C11—C12—C13—C8	−0.7 (4)
C1—N1—C5—C4	1.9 (4)	C9—C8—C13—C12	0.5 (4)
C14—N1—C5—C4	−177.4 (3)	C7—C8—C13—C12	−179.4 (3)
C1—N1—C5—C6	−177.4 (2)	O3—S1—C16—C21	−36.2 (3)
C14—N1—C5—C6	3.3 (4)	O5—S1—C16—C21	83.9 (3)
C3—C4—C5—N1	−1.5 (4)	O4—S1—C16—C21	−156.8 (2)
C3—C4—C5—C6	177.8 (3)	O3—S1—C16—C17	144.8 (3)
N1—C5—C6—C7	−176.7 (3)	O5—S1—C16—C17	−95.2 (3)
C4—C5—C6—C7	4.1 (4)	O4—S1—C16—C17	24.2 (3)
C5—C6—C7—C8	−178.0 (3)	C21—C16—C17—C18	0.0 (4)

C6—C7—C8—C13	−179.1 (3)	S1—C16—C17—C18	179.0 (2)
C6—C7—C8—C9	1.0 (5)	C16—C17—C18—C19	0.4 (5)
C13—C8—C9—C10	0.4 (4)	C17—C18—C19—C20	−0.1 (5)
C7—C8—C9—C10	−179.8 (2)	C17—C18—C19—Br1	177.5 (2)
C15—O1—C10—C9	−0.8 (4)	C18—C19—C20—C21	−0.6 (5)
C15—O1—C10—C11	178.8 (3)	Br1—C19—C20—C21	−178.2 (2)
C8—C9—C10—O1	178.6 (3)	C17—C16—C21—C20	−0.7 (4)
C8—C9—C10—C11	−1.0 (4)	S1—C16—C21—C20	−179.7 (2)
O1—C10—C11—O2	−0.8 (4)	C19—C20—C21—C16	1.0 (4)
C9—C10—C11—O2	178.8 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1*O*2···O1*W*ⁱ	0.82	1.88	2.685 (4)	169
O1*W*—H2*W*1···O4ⁱⁱ	0.81 (5)	2.03 (5)	2.834 (4)	172 (5)
O1*W*—H1*W*1···O3ⁱⁱⁱ	0.81 (4)	1.99 (5)	2.793 (5)	173 (5)
C1—H1*A*···O5ⁱᵛ	0.93	2.57	3.491 (4)	170
C2—H2*A*···O1ᵛ	0.93	2.51	3.440 (4)	176
C2—H2*A*···O2ᵛ	0.93	2.60	3.183 (4)	121
C3—H3*A*···O2ᵛ	0.93	2.54	3.160 (4)	124
C14—H14*A*···O4ⁱᵛ	0.96	2.54	3.448 (5)	158

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