

## 2-[(*E*)-2-(4-Chlorophenyl)ethenyl]-1-methylpyridinium 4-bromobenzene-sulfonate

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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.031;  $wR$  factor = 0.079; data-to-parameter ratio = 33.6.

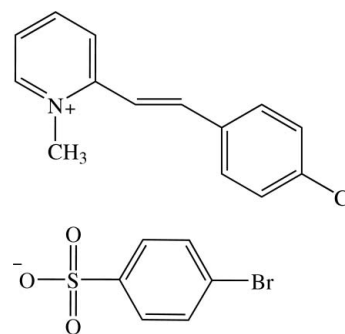
In the title compound,  $\text{C}_{14}\text{H}_{13}\text{ClN}^+\cdot\text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$ , the cation exists in an *E* configuration with respect to the ethenyl bond and is almost planar, the dihedral angle between the pyridinium and the benzene rings being  $2.80$  (7)°. The dihedral angles between the benzene ring of the anion and the pyridinium and benzene rings of the cation are  $80.88$  (7) and  $79.05$  (7)°, respectively. In the crystal, the cations are stacked into columns along the *a* axis as a result of  $\pi$ - $\pi$  interactions between the pyridinium and chlorobenzene rings with a  $Cg \cdots Cg$  distance of  $3.6976$  (8) Å. The anions are linked into chains along the *a* axis by weak  $\text{C}-\text{H} \cdots \text{O}$  interactions. These anion chains are linked to adjacent cations by additional weak  $\text{C}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{Br}$  interactions, forming a two-dimensional network parallel to the *ab* plane. There are also short  $\text{O} \cdots \text{Br}$  [ $3.2567$  (11) Å] and  $\text{C} \cdots \text{O}$  [ $2.9917$  (18) Å] contacts. The crystal structure is further stabilized by  $\text{C}-\text{H} \cdots \pi$  interactions involving the aromatic ring of the anion.

### Related literature

For bond-length data, see: Allen *et al.* (1987). For background to non-linear optical materials research, see: Andreu *et al.* (1999); Jagannathan *et al.* (2007); Cho *et al.* (2002); Lakshmanaperumal *et al.* (2003); Veiros (2001). For related structures, see: Chanawanno *et al.* (2008; 2009); Chantrapromma *et al.* (2006); Fun *et al.* (2009). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).

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### Experimental

#### Crystal data

$\text{C}_{14}\text{H}_{13}\text{ClN}^+\cdot\text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$   
 $M_r = 466.77$   
 Monoclinic,  $P2_1/c$   
 $a = 7.9476$  (1) Å  
 $b = 18.6099$  (3) Å  
 $c = 12.7173$  (2) Å  
 $\beta = 93.467$  (1)°

$V = 1877.50$  (5) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.46$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.51 \times 0.26 \times 0.24$  mm

#### Data collection

Bruker APEXII CCD area-detector diffractometer  
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)  
 $T_{\min} = 0.368$ ,  $T_{\max} = 0.586$   
 (expected range = 0.348–0.554)

36425 measured reflections  
 8227 independent reflections  
 6744 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.079$   
 $S = 1.02$   
 8227 reflections

245 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.73$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ⋯ <i>A</i>	<i>D</i> ⋯ <i>A</i>	<i>D</i> — <i>H</i> ⋯ <i>A</i>
C1—H1A⋯Br <sup>i</sup>	0.93	2.89	3.6585 (14)	141
C3—H3A⋯O3 <sup>iii</sup>	0.93	2.53	3.4285 (17)	163
C6—H6A⋯O2 <sup>iii</sup>	0.93	2.55	3.4702 (17)	172
C7—H7A⋯O1 <sup>iv</sup>	0.93	2.51	3.4057 (17)	161
C13—H13A⋯O2 <sup>iii</sup>	0.93	2.49	3.4205 (17)	180
C14—H14A⋯O1	0.96	2.49	3.3383 (17)	148
C14—H14C⋯O2 <sup>iii</sup>	0.96	2.48	2.9917 (18)	113
C17—H17A⋯O1 <sup>v</sup>	0.93	2.28	3.2110 (17)	175
C20—H20A⋯O1	0.93	2.55	2.9157 (17)	104
C10—H10A⋯Cg3 <sup>vi</sup>	0.93	2.77	3.6831 (16)	169
C12—H12A⋯Cg3 <sup>iii</sup>	0.93	2.79	3.6402 (16)	153

Symmetry codes: (i)  $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (ii)  $-x + 2, -y + 1, -z + 1$ ; (iii)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (iv)  $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x - 1, y, z$ ; (vi)  $-x + 1, -y + 1, -z$ . Cg3 is the centroid of the C15–C20 ring.

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* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2633).

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**supplementary materials**

*Acta Cryst.* (2009). E65, o1884-o1885 [ doi:10.1107/S1600536809026968 ]

## 2-[(*E*)-2-(4-Chlorophenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate

S. Chantrapromma, K. Chanawanno and H.-K. Fun

### Comment

Stilbazolium is a competitive candidate for organic nonlinear optical (NLO) materials and yields high optical nonlinearities including large second harmonic generation (SHG) (Andreu *et al.*, 1999; Jagannathan *et al.*, 2007). Molecules with large  $\pi$  systems have been extensively used in attempts to obtain NLO materials (Veiros, 2001). This hypothesis led to a popular approach towards such materials which are synthesized from compounds with extended  $\pi$  conjugated systems to ensure large second-molecular hyperpolarizability ( $\beta$ ) (Lakshmanaperumal *et al.*, 2003). However, this approach will not be effective if the molecules of these compounds are arranged in centrosymmetric space groups (Cho *et al.*, 2002). The title compound (I) has been synthesized and its crystal structure was undertaken in order to establish the orientation of molecules in the solid state. It was found that (I) crystallized in centrosymmetric space group  $P2_1/c$  so no second-order nonlinear optical properties are observed.

In the molecule of the title compound,  $C_{14}H_{13}CIN^+ \cdot C_6H_4BrO_3S^-$  (Fig. 1), the cation exists in an *E* configuration with respect to the ethenyl C6=C7 bond [1.3393 (19) Å] and the torsion angle of C5–C6–C7–C8 = 178.74 (14)°. The cation is almost planar with the dihedral angle between the pyridinium and benzene rings of the cation being 2.80 (7)°. The anion is inclined to the cation which is reflected by the dihedral angles between the benzene ring of the anion and the pyridinium and benzene rings of the cation being 80.88 (7) and 79.05 (7)°. The Br substituents are coplanar with the attached benzene rings. The bond distances in both cation and anion have normal values (Allen *et al.*, 1987) and are comparable with the closely related compounds (Chanawanno *et al.*, 2008; 2009; Chantrapromma *et al.*, 2006; Fun *et al.*, 2009).

In the crystal packing (Fig. 2), all O atoms of the sulfonate group are involved in weak C—H $\cdots$ O interactions (Table 1). The cations are stacked into columns along the *a* axis as a result of  $\pi$ – $\pi$  interactions with a Cg<sub>1</sub> $\cdots$ Cg<sub>2</sub> distance of 3.6976 (8) Å (symmetry code 2-x, 1-y, -z); Cg<sub>1</sub> and Cg<sub>2</sub> are the centroids of the C1–C5/N1 and C8–C13 rings, respectively. The anions are linked into chains along the *a* axis by a weak C—H $\cdots$ O interaction (Table 1). The anions are linked to the adjacent cations by weak C—H $\cdots$ O and C—H $\cdots$ Br interactions forming a 2D network parallel to the *ab* plane. There are also O $\cdots$ Br [3.2567 (11) Å; symmetry codes: 1+x, 3/2-y, 1/2+z and -1+x, 3/2-y, -1/2+z] and C $\cdots$ O [2.9917 (18) Å; symmetry code: x, 3/2-y, z] short contacts. The crystal structure is further stabilized by C—H $\cdots$  $\pi$  interactions involving the C15–C20 ring of the anion. .

### Experimental

2-[(*E*)-2-(4-Chlorophenyl)ethenyl]-1-methylpyridinium iodide (0.24 g, 0.67 mmol) which was prepared according to a previous report (Chanawanno *et al.*, 2008) was mixed (1:1 molar ratio) with silver(I) 4-bromobenzenesulfonate (0.23 g, 0.67 mmol) (Chantrapromma *et al.*, 2006) in methanol solution (100 ml). The mixture solution was stirred for 30 min, the precipitate of silver iodide which formed was filtered and the filtrate was evaporated to give the title compound as an orange solid. Brown block-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from methanol by slow evaporation at room temperature over a month, Mp. 508-509 K.

## Refinement

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with  $d(\text{C-H}) = 0.93 \text{ \AA}$  for aromatic and CH and  $0.96 \text{ \AA}$  for  $\text{CH}_3$  atoms. The  $U_{\text{iso}}$  values were constrained to be  $1.5U_{\text{eq}}$  of the carrier atom for methyl H atoms and  $1.2U_{\text{eq}}$  for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at  $0.70 \text{ \AA}$  from C11 and the deepest hole is located at  $0.50 \text{ \AA}$  from C11.

## Figures

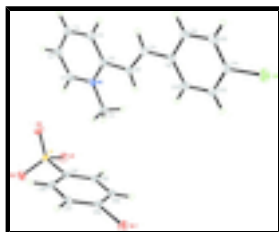


Fig. 1. The molecular structure of the title compound, with 50% probability displacement ellipsoids and the atom-numbering scheme.

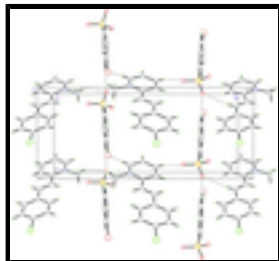


Fig. 2. The crystal packing of the title compound viewed down the  $c$  axis. Weak  $\text{C-H}\cdots\text{O}$  and  $\text{C-H}\cdots\text{Br}$  interactions are shown as dashed lines.

## 2-[(E)-2-(4-Chlorophenyl)ethenyl]-1-methylpyridinium 4-bromobenzenesulfonate

### Crystal data

$\text{C}_{14}\text{H}_{13}\text{ClN}^+\cdot\text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$

$M_r = 466.77$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 7.9476 (1) \text{ \AA}$

$b = 18.6099 (3) \text{ \AA}$

$c = 12.7173 (2) \text{ \AA}$

$\beta = 93.467 (1)^\circ$

$V = 1877.50 (5) \text{ \AA}^3$

$Z = 4$

$F_{000} = 944$

$D_x = 1.651 \text{ Mg m}^{-3}$

Melting point =  $508\text{--}509 \text{ K}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8227 reflections

$\theta = 2.2\text{--}35.0^\circ$

$\mu = 2.46 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, brown

$0.51 \times 0.26 \times 0.24 \text{ mm}$

### Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: sealed tube

Monochromator: graphite

8227 independent reflections

6744 reflections with  $I > 2\sigma(I)$

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

$T = 100$ K	$\theta_{\max} = 35.0^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\min} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$h = -12 \rightarrow 12$
$T_{\min} = 0.368$ , $T_{\max} = 0.586$	$k = -29 \rightarrow 30$
36425 measured reflections	$l = -20 \rightarrow 20$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.031$	H-atom parameters constrained
$wR(F^2) = 0.079$	$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 1.227P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
8227 reflections	$(\Delta/\sigma)_{\max} = 0.002$
245 parameters	$\Delta\rho_{\max} = 1.30 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.73 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

### 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 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.** 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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.233790 (18)	0.807999 (8)	0.089929 (11)	0.01901 (4)
Cl1	0.39854 (5)	0.44980 (2)	-0.33199 (3)	0.02829 (8)
S1	0.87153 (4)	0.769209 (17)	0.42302 (2)	0.01344 (6)
N1	1.03961 (15)	0.57489 (6)	0.26973 (9)	0.0163 (2)
O1	1.01963 (13)	0.79162 (6)	0.36935 (9)	0.01957 (19)
O2	0.83179 (15)	0.81603 (6)	0.50948 (8)	0.0220 (2)
O3	0.87526 (14)	0.69338 (5)	0.45166 (8)	0.01917 (19)
C1	1.1310 (2)	0.57574 (8)	0.36310 (11)	0.0206 (3)
H1A	1.1703	0.6194	0.3904	0.025*

## supplementary materials

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C2	1.1670 (2)	0.51371 (8)	0.41839 (11)	0.0219 (3)
H2A	1.2302	0.5150	0.4823	0.026*
C3	1.1070 (2)	0.44893 (8)	0.37682 (11)	0.0214 (3)
H3A	1.1279	0.4063	0.4134	0.026*
C4	1.01612 (19)	0.44842 (8)	0.28073 (11)	0.0195 (2)
H4A	0.9780	0.4050	0.2521	0.023*
C5	0.98054 (17)	0.51241 (7)	0.22572 (11)	0.0163 (2)
C6	0.88146 (18)	0.51613 (7)	0.12614 (11)	0.0180 (2)
H6A	0.8578	0.5612	0.0973	0.022*
C7	0.82227 (19)	0.45815 (7)	0.07362 (11)	0.0191 (2)
H7A	0.8488	0.4134	0.1027	0.023*
C8	0.71911 (18)	0.45944 (7)	-0.02595 (11)	0.0166 (2)
C9	0.6540 (2)	0.39406 (7)	-0.06589 (11)	0.0207 (3)
H9A	0.6790	0.3518	-0.0293	0.025*
C10	0.5528 (2)	0.39117 (8)	-0.15891 (12)	0.0225 (3)
H10A	0.5082	0.3477	-0.1836	0.027*
C11	0.51988 (19)	0.45417 (8)	-0.21391 (11)	0.0193 (2)
C12	0.58160 (19)	0.52002 (8)	-0.17711 (11)	0.0193 (2)
H12A	0.5572	0.5619	-0.2149	0.023*
C13	0.68025 (18)	0.52247 (7)	-0.08315 (11)	0.0184 (2)
H13A	0.7211	0.5664	-0.0578	0.022*
C14	1.0017 (2)	0.64493 (7)	0.21800 (11)	0.0202 (3)
H14A	1.0547	0.6828	0.2591	0.030*
H14B	0.8820	0.6524	0.2126	0.030*
H14C	1.0439	0.6449	0.1488	0.030*
C15	0.69849 (16)	0.77983 (7)	0.32849 (10)	0.0132 (2)
C16	0.53518 (17)	0.77816 (7)	0.36296 (10)	0.0166 (2)
H16A	0.5188	0.7707	0.4339	0.020*
C17	0.39682 (17)	0.78748 (7)	0.29222 (11)	0.0162 (2)
H17A	0.2879	0.7859	0.3150	0.019*
C18	0.42424 (17)	0.79926 (7)	0.18665 (10)	0.0146 (2)
C19	0.58535 (18)	0.80181 (7)	0.15040 (10)	0.0150 (2)
H19A	0.6012	0.8102	0.0796	0.018*
C20	0.72348 (17)	0.79154 (7)	0.22238 (10)	0.0139 (2)
H20A	0.8323	0.7925	0.1993	0.017*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01657 (7)	0.02094 (6)	0.01858 (6)	0.00174 (5)	-0.00664 (5)	0.00000 (5)
Cl1	0.02706 (18)	0.0357 (2)	0.02110 (15)	0.00237 (15)	-0.00652 (13)	-0.00412 (14)
S1	0.01243 (13)	0.01367 (12)	0.01385 (12)	0.00116 (10)	-0.00235 (10)	-0.00005 (9)
N1	0.0170 (5)	0.0155 (5)	0.0163 (5)	0.0024 (4)	0.0002 (4)	-0.0001 (4)
O1	0.0124 (4)	0.0235 (5)	0.0225 (5)	-0.0018 (4)	-0.0013 (4)	0.0022 (4)
O2	0.0244 (5)	0.0241 (5)	0.0169 (4)	0.0055 (4)	-0.0041 (4)	-0.0065 (4)
O3	0.0203 (5)	0.0150 (4)	0.0215 (4)	0.0013 (4)	-0.0043 (4)	0.0040 (3)
C1	0.0247 (7)	0.0205 (6)	0.0162 (5)	0.0026 (5)	-0.0010 (5)	-0.0015 (4)
C2	0.0251 (7)	0.0248 (6)	0.0154 (5)	0.0050 (5)	-0.0009 (5)	0.0015 (5)

C3	0.0249 (7)	0.0205 (6)	0.0190 (6)	0.0057 (5)	0.0023 (5)	0.0034 (5)
C4	0.0209 (6)	0.0164 (5)	0.0212 (6)	0.0017 (5)	0.0007 (5)	0.0013 (4)
C5	0.0153 (6)	0.0161 (5)	0.0173 (5)	0.0026 (4)	-0.0003 (4)	0.0000 (4)
C6	0.0196 (6)	0.0169 (5)	0.0171 (5)	0.0012 (5)	-0.0020 (5)	0.0007 (4)
C7	0.0226 (6)	0.0170 (6)	0.0176 (5)	0.0008 (5)	0.0003 (5)	0.0013 (4)
C8	0.0169 (6)	0.0146 (5)	0.0183 (5)	-0.0003 (4)	-0.0001 (4)	-0.0001 (4)
C9	0.0261 (7)	0.0141 (5)	0.0217 (6)	-0.0008 (5)	-0.0021 (5)	-0.0002 (4)
C10	0.0278 (7)	0.0174 (6)	0.0220 (6)	-0.0026 (5)	-0.0016 (5)	-0.0034 (5)
C11	0.0186 (6)	0.0221 (6)	0.0170 (5)	0.0015 (5)	-0.0004 (5)	-0.0023 (4)
C12	0.0197 (6)	0.0176 (6)	0.0203 (6)	0.0012 (5)	-0.0014 (5)	0.0018 (4)
C13	0.0182 (6)	0.0144 (5)	0.0223 (6)	-0.0009 (4)	-0.0008 (5)	0.0004 (4)
C14	0.0268 (7)	0.0143 (5)	0.0191 (6)	0.0023 (5)	-0.0032 (5)	0.0006 (4)
C15	0.0131 (5)	0.0127 (5)	0.0137 (5)	0.0005 (4)	-0.0008 (4)	0.0000 (4)
C16	0.0145 (5)	0.0206 (6)	0.0146 (5)	0.0016 (5)	0.0002 (4)	0.0018 (4)
C17	0.0126 (5)	0.0194 (5)	0.0166 (5)	0.0012 (4)	-0.0004 (4)	0.0010 (4)
C18	0.0136 (5)	0.0140 (5)	0.0156 (5)	0.0011 (4)	-0.0036 (4)	-0.0003 (4)
C19	0.0175 (6)	0.0146 (5)	0.0127 (5)	0.0004 (4)	-0.0011 (4)	-0.0006 (4)
C20	0.0132 (5)	0.0143 (5)	0.0141 (5)	0.0006 (4)	0.0003 (4)	-0.0002 (4)

*Geometric parameters (Å, °)*

Br1—C18	1.8988 (13)	C8—C9	1.4052 (19)
Cl1—C11	1.7368 (14)	C9—C10	1.390 (2)
S1—O2	1.4525 (11)	C9—H9A	0.9300
S1—O1	1.4569 (11)	C10—C11	1.382 (2)
S1—O3	1.4572 (10)	C10—H10A	0.9300
S1—C15	1.7820 (13)	C11—C12	1.390 (2)
N1—C1	1.3540 (18)	C12—C13	1.390 (2)
N1—C5	1.3615 (18)	C12—H12A	0.9300
N1—C14	1.4828 (17)	C13—H13A	0.9300
C1—C2	1.373 (2)	C14—H14A	0.9600
C1—H1A	0.9300	C14—H14B	0.9600
C2—C3	1.389 (2)	C14—H14C	0.9600
C2—H2A	0.9300	C15—C20	1.3930 (18)
C3—C4	1.381 (2)	C15—C16	1.3952 (19)
C3—H3A	0.9300	C16—C17	1.3889 (18)
C4—C5	1.4013 (19)	C16—H16A	0.9300
C4—H4A	0.9300	C17—C18	1.3905 (19)
C5—C6	1.4518 (19)	C17—H17A	0.9300
C6—C7	1.3393 (19)	C18—C19	1.3877 (19)
C6—H6A	0.9300	C19—C20	1.3993 (18)
C7—C8	1.4665 (19)	C19—H19A	0.9300
C7—H7A	0.9300	C20—H20A	0.9300
C8—C13	1.4048 (19)		
O2—S1—O1	113.69 (7)	C11—C10—C9	118.67 (13)
O2—S1—O3	113.19 (7)	C11—C10—H10A	120.7
O1—S1—O3	112.92 (7)	C9—C10—H10A	120.7
O2—S1—C15	104.47 (6)	C10—C11—C12	121.67 (13)
O1—S1—C15	105.34 (6)	C10—C11—Cl1	118.43 (11)



## supplementary materials

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O3—S1—C15	106.22 (6)	C12—C11—C11	119.90 (11)
C1—N1—C5	121.59 (12)	C13—C12—C11	119.18 (13)
C1—N1—C14	117.56 (12)	C13—C12—H12A	120.4
C5—N1—C14	120.84 (11)	C11—C12—H12A	120.4
N1—C1—C2	121.57 (14)	C12—C13—C8	120.85 (13)
N1—C1—H1A	119.2	C12—C13—H13A	119.6
C2—C1—H1A	119.2	C8—C13—H13A	119.6
C1—C2—C3	118.61 (13)	N1—C14—H14A	109.5
C1—C2—H2A	120.7	N1—C14—H14B	109.5
C3—C2—H2A	120.7	H14A—C14—H14B	109.5
C4—C3—C2	119.44 (13)	N1—C14—H14C	109.5
C4—C3—H3A	120.3	H14A—C14—H14C	109.5
C2—C3—H3A	120.3	H14B—C14—H14C	109.5
C3—C4—C5	120.98 (13)	C20—C15—C16	119.85 (12)
C3—C4—H4A	119.5	C20—C15—S1	121.43 (10)
C5—C4—H4A	119.5	C16—C15—S1	118.70 (9)
N1—C5—C4	117.80 (12)	C17—C16—C15	120.59 (12)
N1—C5—C6	118.24 (12)	C17—C16—H16A	119.7
C4—C5—C6	123.95 (13)	C15—C16—H16A	119.7
C7—C6—C5	123.52 (13)	C16—C17—C18	118.74 (13)
C7—C6—H6A	118.2	C16—C17—H17A	120.6
C5—C6—H6A	118.2	C18—C17—H17A	120.6
C6—C7—C8	125.35 (13)	C19—C18—C17	121.86 (12)
C6—C7—H7A	117.3	C19—C18—Br1	119.82 (10)
C8—C7—H7A	117.3	C17—C18—Br1	118.27 (10)
C13—C8—C9	118.10 (12)	C18—C19—C20	118.76 (12)
C13—C8—C7	123.69 (12)	C18—C19—H19A	120.6
C9—C8—C7	118.20 (12)	C20—C19—H19A	120.6
C10—C9—C8	121.50 (13)	C15—C20—C19	120.19 (12)
C10—C9—H9A	119.3	C15—C20—H20A	119.9
C8—C9—H9A	119.3	C19—C20—H20A	119.9
C5—N1—C1—C2	-0.7 (2)	C10—C11—C12—C13	0.6 (2)
C14—N1—C1—C2	177.66 (14)	C11—C11—C12—C13	-179.20 (11)
N1—C1—C2—C3	-0.2 (2)	C11—C12—C13—C8	0.6 (2)
C1—C2—C3—C4	1.2 (2)	C9—C8—C13—C12	-0.7 (2)
C2—C3—C4—C5	-1.4 (2)	C7—C8—C13—C12	-179.97 (14)
C1—N1—C5—C4	0.5 (2)	O2—S1—C15—C20	132.62 (11)
C14—N1—C5—C4	-177.77 (13)	O1—S1—C15—C20	12.55 (12)
C1—N1—C5—C6	179.13 (13)	O3—S1—C15—C20	-107.47 (11)
C14—N1—C5—C6	0.8 (2)	O2—S1—C15—C16	-45.68 (12)
C3—C4—C5—N1	0.5 (2)	O1—S1—C15—C16	-165.75 (11)
C3—C4—C5—C6	-178.01 (14)	O3—S1—C15—C16	74.23 (12)
N1—C5—C6—C7	177.40 (14)	C20—C15—C16—C17	0.5 (2)
C4—C5—C6—C7	-4.1 (2)	S1—C15—C16—C17	178.87 (11)
C5—C6—C7—C8	178.74 (14)	C15—C16—C17—C18	-0.7 (2)
C6—C7—C8—C13	5.2 (2)	C16—C17—C18—C19	0.1 (2)
C6—C7—C8—C9	-174.16 (15)	C16—C17—C18—Br1	177.48 (10)
C13—C8—C9—C10	-0.4 (2)	C17—C18—C19—C20	0.59 (19)
C7—C8—C9—C10	178.93 (14)	Br1—C18—C19—C20	-176.75 (9)

C8—C9—C10—C11	1.6 (2)	C16—C15—C20—C19	0.17 (19)
C9—C10—C11—C12	-1.7 (2)	S1—C15—C20—C19	-178.11 (10)
C9—C10—C11—C11	178.16 (12)	C18—C19—C20—C15	-0.72 (19)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C1—H1A $\cdots$ Br1 <sup>i</sup>	0.93	2.89	3.6585 (14)	141
C3—H3A $\cdots$ O3 <sup>ii</sup>	0.93	2.53	3.4285 (17)	163
C6—H6A $\cdots$ O2 <sup>iii</sup>	0.93	2.55	3.4702 (17)	172
C7—H7A $\cdots$ O1 <sup>iv</sup>	0.93	2.51	3.4057 (17)	161
C13—H13A $\cdots$ O2 <sup>iii</sup>	0.93	2.49	3.4205 (17)	180
C14—H14A $\cdots$ O1	0.96	2.49	3.3383 (17)	148
C14—H14C $\cdots$ O2 <sup>iii</sup>	0.96	2.48	2.9917 (18)	113
C17—H17A $\cdots$ O1 <sup>v</sup>	0.93	2.28	3.2110 (17)	175
C20—H20A $\cdots$ O1	0.93	2.55	2.9157 (17)	104
C10—H10A $\cdots$ Cg3 <sup>vi</sup>	0.93	2.77	3.6831 (16)	169
C12—H12A $\cdots$ Cg3 <sup>iii</sup>	0.93	2.79	3.6402 (16)	153

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

Fig. 1

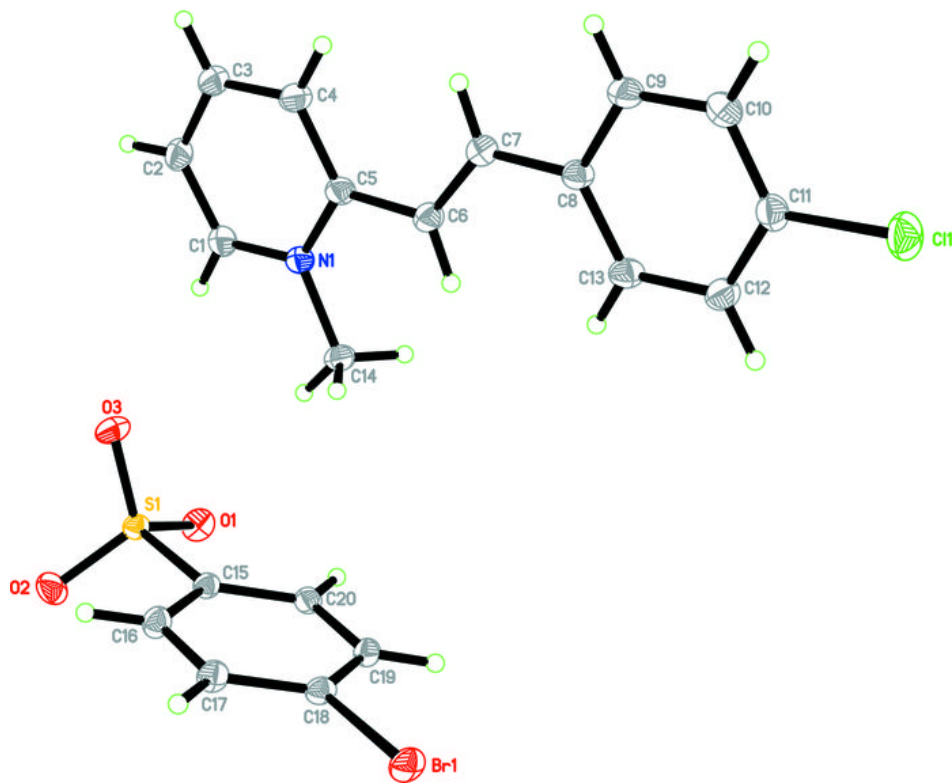


Fig. 2

