

# 1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]-quinolinium 4-bromobenzenesulfonate

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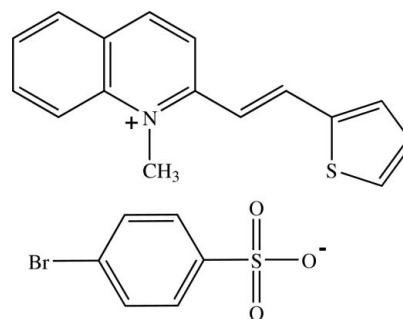
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.089; data-to-parameter ratio = 22.2.

In the title compound,  $\text{C}_{16}\text{H}_{14}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$ , the cation exists in an *E* configuration and is essentially planar, the dihedral angle between the quinolinium and thiophene rings being  $3.45(9)^\circ$ . The anion is inclined to the cation with dihedral angles of  $75.43(8)$  and  $72.03(11)^\circ$ , respectively between the benzene ring and the quinolinium and thiophene rings. In the crystal, the cations and anions are arranged individually into separate chains along the *c* axis. The cation chains are stacked in an antiparallel manner along the *a* axis by  $\pi\cdots\pi$  interactions with centroid-centroid distances of  $3.7257(13)$  and  $3.7262(14)$  Å. Weak  $\text{C}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\pi$  interactions link the cations and anions into a three-dimensional network. Short  $\text{Br}\cdots\text{S}$  [ $3.7224(5)$  Å] and  $\text{Br}\cdots\text{O}$  [ $3.4267(16)$  Å] contacts are also observed.

## Related literature

For bond-length data, see: Allen *et al.* (1987). For background to non-linear optical materials research, see: Chantrapromma *et al.* (2009*a,b*), Fun *et al.* (2009); Raimundo *et al.* (2002). For related structures, see: Chantrapromma *et al.* (2006); Ruanwas *et al.* (2008). For the stability of the temperature controller used in the data collection, see Cosier & Glazer, (1986).



## Experimental

### Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$   
 $M_r = 488.41$   
 Monoclinic,  $P2_1/c$   
 $a = 7.9026(1)$  Å  
 $b = 18.8211(2)$  Å  
 $c = 13.4816(1)$  Å  
 $\beta = 93.292(1)^\circ$   
 $V = 2001.89(4)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.29$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.34 \times 0.32 \times 0.24$  mm

### Data collection

Bruker APEXII CCD area detector  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2005)  
 $T_{\min} = 0.511$ ,  $T_{\max} = 0.612$   
 51446 measured reflections  
 5827 independent reflections  
 5163 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.089$   
 $S = 1.12$   
 5827 reflections  
 263 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>

## Table 1

Hydrogen-bond geometry (Å, °).

*Cg*4 is the centroid of the C17–C22 benzene ring.

<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>
C3–H3A $\cdots$ O3 <sup>i</sup>	0.93	2.51	3.409 (3)	162
C7–H7A $\cdots$ O1 <sup>iii</sup>	0.93	2.47	3.241 (3)	140
C8–H8A $\cdots$ O2 <sup>iii</sup>	0.93	2.29	3.218 (3)	175
C10–H10A $\cdots$ S1	0.93	2.77	3.185 (2)	108
C11–H11A $\cdots$ O2 <sup>iii</sup>	0.93	2.31	3.238 (3)	176
C15–H15A $\cdots$ O3 <sup>iv</sup>	0.93	2.40	3.265 (3)	154
C16–H16B $\cdots$ O1 <sup>v</sup>	0.96	2.43	3.321 (3)	155
C17–H17A $\cdots$ O1	0.93	2.54	2.915 (3)	105
C20–H20A $\cdots$ O1 <sup>vi</sup>	0.93	2.32	3.242 (3)	172
C13–H13A $\cdots$ <i>Cg</i> 4 <sup>iii</sup>	0.93	2.57	3.434 (2)	155

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

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: SJ2736).

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**supplementary materials**

*Acta Cryst.* (2010). E66, o1053-o1054 [ doi:10.1107/S1600536810007488 ]

## 1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

H.-K. Fun, T. Kobkeatthawin and S. Chantrapromma

### Comment

During the course of our NLO (non-linear optical) materials research, we have previously reported the crystal structures of the NLO-active compounds (Chantrapromma *et al.*, 2009*a, b*; Fun *et al.*, 2009). With the knowledge that the organic dipolar compounds with extended  $\pi$  systems and having terminal donor and acceptor groups are likely to exhibit large hyperpolarizability ( $\beta$ ) (Raimundo *et al.*, 2002), the title compound (I) was designed and synthesized in order to study its NLO properties. Unfortunately (I) crystallizes out in a centrosymmetric  $P2_1/c$  space group which precluded the second-order nonlinear optical properties.

The asymmetric unit of the title compound (Fig. 1) consists of the  $C_{16}H_{14}NS^+$  cation and  $C_6H_4BrO_3S^-$  anion. The cation exists in the *E* configuration with respect to the C10=C11 double bond [1.348 (3) Å] and is essentially planar with the dihedral angle between the quinolinium and the thiophene rings being 3.45 (9)° and the torsion angles C9–C10–C11–C12 = -179.8 (2)°. The ten non-H atoms of quinolinium unit lie on the same plane with an r.m.s. deviation of 0.0184 (2) Å. The relative arrangement of cation and anion is shown by the angles between the mean plane of the 4-bromophenyl ring and those of the quinolinium and thiophene rings which are 75.43 (8)° and 72.03 (11)°, respectively. The bond lengths are normal (Allen *et al.*, 1987) and are comparable with those in related structures (Chantrapromma *et al.*, 2006; Ruanwas *et al.*, 2008).

In the crystal, all O atoms of sulfonate group are involved in weak C—H $\cdots$ O interactions (Table 1). The cations and anions are arranged individually into chains along the *c* axis (Fig. 2). The cation chains are stacked in an antiparallel manner along the *a* axis by  $\pi$ – $\pi$  interactions with  $Cg_1\cdots Cg_2 = 3.7257$  (13) Å (symmetry code: -x, -y, 1-z) and  $Cg_1\cdots Cg_3 = 3.7262$  (14) Å (symmetry code: 1-x, -y, 1-z);  $Cg_1$ ,  $Cg_2$  and  $Cg_3$  are the centroids of the S1/C12–C15, N1/C1/C6–C9 and C1–C6 rings, respectively. Weak C—H $\cdots$ O and C—H $\cdots$  $\pi$  interactions (Table 1) link the cations and anions into a three-dimensional network;  $Cg_4$  is the centroid of the C17–C22 benzene ring. Short Br $\cdots$ S [3.7224 (5) Å] and Br $\cdots$ O [3.4267 (16) Å] contacts (symmetry code for both: 1+x, 1/2-y, 1/2+z) are also observed.

### Experimental

2-(2-Thiophenestyryl)-1-methylquinolinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,2-dimethylquinolinium iodide (2.00 g, 7.0 mmol), 2-thiophenecarboxaldehyde (0.64 ml, 7.0 mmol) and piperidine (0.69 ml, 7.0 mmol) in hot methanol (40 ml). The resulting solution was refluxed for 5 h under nitrogen atmosphere. The resultant solid was filtered off and washed with diethyl ether. Silver(I)4-bromobenzenesulfonate (compound B) was synthesized according to our previously reported procedure. (Chantrapromma *et al.*, 2006). The title compound was synthesized by mixing compound A (0.10 g, 0.26 mmol) in hot methanol (50 ml) and compound B (0.09 g, 0.26 mmol) in hot methanol (20 ml). The mixture immediately yielded a grey precipitate of silver iodide. After stirring the mixture for ca. 45 min, the precipitate was removed and the resulting solution was evaporated yielding a brown solid. Brown block-shaped single crystals of the title compound suitable for *x*-ray diffraction analysis were recrystallized from methanol solvent by slow evaporation at room temperature over a few weeks. (Mp. 538–539 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  $0.75 \text{ \AA}$  from Br1 and the deepest hole is located at  $0.55 \text{ \AA}$  from S1.

## Figures

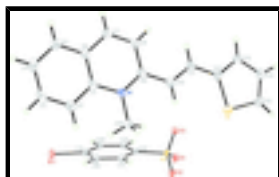


Fig. 1. The molecular structure of the title compound, with 50% probability displacement ellipsoids and the atom-numbering scheme.

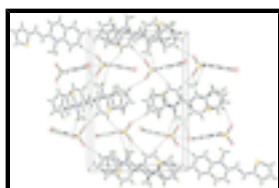


Fig. 2. The crystal packing of the title compound viewed down the  $a$  axis. Hydrogen bonds and weak  $\text{C—H}\cdots\text{O}$  interactions are shown as dashed lines.

## 1-Methyl-2-[(*E*)-2-(2-thienyl)ethenyl]quinolinium 4-bromobenzenesulfonate

### Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+ \cdot \text{C}_6\text{H}_4\text{BrO}_3\text{S}^-$

$M_r = 488.41$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 7.9026 (1) \text{ \AA}$

$b = 18.8211 (2) \text{ \AA}$

$c = 13.4816 (1) \text{ \AA}$

$\beta = 93.292 (1)^\circ$

$V = 2001.89 (4) \text{ \AA}^3$

$Z = 4$

$F(000) = 992$

$D_x = 1.620 \text{ Mg m}^{-3}$

Melting point =  $538\text{--}539 \text{ K}$

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

Cell parameters from 5827 reflections

$\theta = 2.2\text{--}30.0^\circ$

$\mu = 2.29 \text{ mm}^{-1}$

$T = 100 \text{ K}$

Block, brown

$0.34 \times 0.32 \times 0.24 \text{ mm}$

### Data collection

Bruker APEXII CCD area detector diffractometer

Radiation source: sealed tube graphite

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\text{min}} = 0.511$ ,  $T_{\text{max}} = 0.612$

5827 independent reflections

5163 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 30.0^\circ$ ,  $\theta_{\text{min}} = 2.2^\circ$

$h = -11 \rightarrow 11$

$k = -26 \rightarrow 26$

51446 measured reflections

$l = -18 \rightarrow 18$

### Refinement

Refinement on  $F^2$

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.035$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.089$

H-atom parameters constrained

$S = 1.12$

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 3.2344P]$

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

5827 reflections

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

263 parameters

$\Delta\rho_{\max} = 1.18 \text{ e } \text{\AA}^{-3}$

0 restraints

$\Delta\rho_{\min} = -0.46 \text{ e } \text{\AA}^{-3}$

### 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 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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.00270 (7)	0.06224 (3)	0.28565 (4)	0.02261 (11)
N1	0.3667 (2)	0.04462 (9)	0.63104 (13)	0.0179 (3)
C1	0.4567 (3)	0.03115 (11)	0.72171 (15)	0.0178 (4)
C2	0.4926 (3)	0.08556 (12)	0.79170 (16)	0.0219 (4)
H2A	0.4584	0.1320	0.7780	0.026*
C3	0.5783 (3)	0.06935 (13)	0.87999 (17)	0.0246 (4)
H3A	0.6020	0.1053	0.9260	0.030*
C4	0.6314 (3)	-0.00053 (14)	0.90275 (17)	0.0257 (5)
H4A	0.6896	-0.0104	0.9631	0.031*
C5	0.5967 (3)	-0.05415 (12)	0.83528 (16)	0.0220 (4)
H5A	0.6308	-0.1004	0.8501	0.026*
C6	0.5094 (3)	-0.03885 (11)	0.74348 (15)	0.0185 (4)
C7	0.4708 (3)	-0.09311 (11)	0.67292 (16)	0.0198 (4)
H7A	0.5081	-0.1393	0.6856	0.024*
C8	0.3799 (3)	-0.07819 (11)	0.58700 (16)	0.0204 (4)

## supplementary materials

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H8A	0.3542	-0.1143	0.5415	0.025*
C9	0.3237 (3)	-0.00778 (11)	0.56601 (15)	0.0179 (4)
C10	0.2217 (3)	0.00785 (12)	0.47635 (16)	0.0217 (4)
H10A	0.1787	0.0537	0.4692	0.026*
C11	0.1837 (3)	-0.03853 (11)	0.40215 (16)	0.0197 (4)
H11A	0.2259	-0.0845	0.4089	0.024*
C12	0.0821 (3)	-0.02164 (11)	0.31320 (16)	0.0197 (4)
C13	0.0397 (3)	-0.06890 (11)	0.23773 (17)	0.0210 (4)
H13A	0.0709	-0.1166	0.2387	0.025*
C14	-0.0574 (3)	-0.03622 (13)	0.15811 (18)	0.0261 (5)
H14A	-0.0965	-0.0603	0.1010	0.031*
C15	-0.0870 (3)	0.03424 (13)	0.17442 (18)	0.0258 (5)
H15A	-0.1489	0.0635	0.1301	0.031*
C16	0.3192 (3)	0.11898 (12)	0.60670 (18)	0.0254 (5)
H16A	0.3170	0.1256	0.5360	0.038*
H16B	0.4009	0.1507	0.6383	0.038*
H16C	0.2091	0.1288	0.6300	0.038*
Br1	1.28408 (3)	0.278131 (13)	0.464999 (17)	0.02491 (7)
S2	0.66919 (6)	0.23502 (2)	0.13641 (3)	0.01276 (9)
O1	0.51250 (19)	0.23380 (8)	0.18823 (12)	0.0197 (3)
O2	0.6865 (2)	0.29873 (8)	0.07625 (11)	0.0202 (3)
O3	0.7004 (2)	0.16993 (8)	0.08184 (11)	0.0211 (3)
C17	0.8027 (3)	0.25412 (11)	0.32873 (15)	0.0177 (4)
H17A	0.6913	0.2560	0.3474	0.021*
C18	0.9364 (3)	0.26436 (12)	0.39958 (15)	0.0203 (4)
H18A	0.9153	0.2731	0.4656	0.024*
C19	1.1011 (3)	0.26130 (11)	0.36972 (15)	0.0174 (4)
C20	1.1376 (3)	0.24670 (11)	0.27242 (16)	0.0173 (4)
H20A	1.2492	0.2436	0.2544	0.021*
C21	1.0033 (3)	0.23684 (10)	0.20250 (15)	0.0161 (4)
H21A	1.0251	0.2274	0.1367	0.019*
C22	0.8362 (2)	0.24106 (10)	0.23020 (14)	0.0141 (3)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
S1	0.0243 (3)	0.0173 (2)	0.0262 (3)	0.00428 (19)	0.0006 (2)	0.00228 (19)
N1	0.0176 (8)	0.0160 (8)	0.0201 (8)	-0.0014 (6)	0.0019 (6)	-0.0001 (6)
C1	0.0151 (9)	0.0204 (9)	0.0182 (9)	-0.0018 (7)	0.0033 (7)	-0.0004 (7)
C2	0.0207 (10)	0.0209 (10)	0.0243 (10)	-0.0012 (8)	0.0026 (8)	-0.0038 (8)
C3	0.0239 (11)	0.0281 (11)	0.0220 (10)	-0.0047 (9)	0.0020 (8)	-0.0083 (8)
C4	0.0229 (11)	0.0358 (12)	0.0183 (10)	-0.0039 (9)	0.0000 (8)	0.0013 (9)
C5	0.0206 (10)	0.0230 (10)	0.0226 (10)	-0.0011 (8)	0.0026 (8)	0.0053 (8)
C6	0.0170 (9)	0.0211 (10)	0.0177 (9)	-0.0025 (7)	0.0035 (7)	0.0001 (7)
C7	0.0218 (10)	0.0154 (9)	0.0222 (10)	-0.0007 (7)	0.0026 (8)	0.0016 (7)
C8	0.0235 (10)	0.0160 (9)	0.0217 (10)	-0.0026 (8)	0.0013 (8)	-0.0030 (7)
C9	0.0176 (9)	0.0173 (9)	0.0189 (9)	-0.0023 (7)	0.0027 (7)	0.0001 (7)
C10	0.0237 (10)	0.0192 (9)	0.0221 (10)	0.0007 (8)	0.0007 (8)	0.0001 (8)

C11	0.0191 (10)	0.0179 (9)	0.0222 (10)	0.0000 (7)	0.0021 (8)	0.0020 (7)
C12	0.0178 (9)	0.0180 (9)	0.0232 (10)	0.0002 (7)	0.0002 (8)	0.0040 (8)
C13	0.0195 (10)	0.0158 (9)	0.0279 (11)	-0.0001 (7)	0.0024 (8)	0.0010 (8)
C14	0.0260 (11)	0.0250 (11)	0.0266 (11)	-0.0017 (9)	-0.0039 (9)	0.0001 (9)
C15	0.0219 (10)	0.0273 (11)	0.0274 (11)	0.0046 (9)	-0.0056 (8)	0.0065 (9)
C16	0.0293 (11)	0.0152 (9)	0.0310 (11)	-0.0001 (8)	-0.0046 (9)	-0.0004 (8)
Br1	0.02009 (11)	0.03105 (12)	0.02239 (11)	-0.00586 (8)	-0.00934 (8)	0.00605 (8)
S2	0.0121 (2)	0.0129 (2)	0.01296 (19)	-0.00040 (15)	-0.00194 (15)	0.00143 (15)
O1	0.0130 (7)	0.0228 (7)	0.0230 (7)	-0.0007 (5)	-0.0006 (5)	0.0033 (6)
O2	0.0221 (7)	0.0189 (7)	0.0193 (7)	-0.0012 (6)	-0.0031 (6)	0.0072 (6)
O3	0.0228 (7)	0.0187 (7)	0.0211 (7)	0.0018 (6)	-0.0048 (6)	-0.0048 (6)
C17	0.0147 (9)	0.0231 (10)	0.0156 (9)	-0.0020 (7)	0.0022 (7)	0.0008 (7)
C18	0.0206 (10)	0.0269 (10)	0.0132 (8)	-0.0032 (8)	-0.0004 (7)	0.0011 (7)
C19	0.0141 (9)	0.0196 (9)	0.0178 (9)	-0.0032 (7)	-0.0058 (7)	0.0041 (7)
C20	0.0118 (8)	0.0178 (9)	0.0221 (9)	0.0002 (7)	-0.0001 (7)	0.0030 (7)
C21	0.0153 (9)	0.0168 (9)	0.0164 (8)	-0.0001 (7)	0.0016 (7)	0.0003 (7)
C22	0.0138 (8)	0.0123 (8)	0.0160 (8)	-0.0005 (6)	-0.0014 (7)	0.0008 (6)

*Geometric parameters (Å, °)*

S1—C15	1.705 (2)	C12—C13	1.378 (3)
S1—C12	1.731 (2)	C13—C14	1.423 (3)
N1—C9	1.350 (3)	C13—H13A	0.9300
N1—C1	1.402 (3)	C14—C15	1.367 (3)
N1—C16	1.481 (3)	C14—H14A	0.9300
C1—C6	1.407 (3)	C15—H15A	0.9300
C1—C2	1.410 (3)	C16—H16A	0.9600
C2—C3	1.370 (3)	C16—H16B	0.9600
C2—H2A	0.9300	C16—H16C	0.9600
C3—C4	1.409 (4)	Br1—C19	1.9050 (19)
C3—H3A	0.9300	S2—O1	1.4565 (16)
C4—C5	1.376 (3)	S2—O3	1.4572 (15)
C4—H4A	0.9300	S2—O2	1.4585 (15)
C5—C6	1.412 (3)	S2—C22	1.778 (2)
C5—H5A	0.9300	C17—C22	1.391 (3)
C6—C7	1.417 (3)	C17—C18	1.396 (3)
C7—C8	1.357 (3)	C17—H17A	0.9300
C7—H7A	0.9300	C18—C19	1.385 (3)
C8—C9	1.421 (3)	C18—H18A	0.9300
C8—H8A	0.9300	C19—C20	1.387 (3)
C9—C10	1.444 (3)	C20—C21	1.391 (3)
C10—C11	1.348 (3)	C20—H20A	0.9300
C10—H10A	0.9300	C21—C22	1.395 (3)
C11—C12	1.440 (3)	C21—H21A	0.9300
C11—H11A	0.9300		
C15—S1—C12	91.95 (11)	C12—C13—C14	112.1 (2)
C9—N1—C1	122.04 (18)	C12—C13—H13A	124.0
C9—N1—C16	119.69 (18)	C14—C13—H13A	124.0
C1—N1—C16	118.27 (18)	C15—C14—C13	112.8 (2)



## supplementary materials

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N1—C1—C6	118.71 (18)	C15—C14—H14A	123.6
N1—C1—C2	121.65 (19)	C13—C14—H14A	123.6
C6—C1—C2	119.6 (2)	C14—C15—S1	112.02 (17)
C3—C2—C1	119.4 (2)	C14—C15—H15A	124.0
C3—C2—H2A	120.3	S1—C15—H15A	124.0
C1—C2—H2A	120.3	N1—C16—H16A	109.5
C2—C3—C4	121.6 (2)	N1—C16—H16B	109.5
C2—C3—H3A	119.2	H16A—C16—H16B	109.5
C4—C3—H3A	119.2	N1—C16—H16C	109.5
C5—C4—C3	119.7 (2)	H16A—C16—H16C	109.5
C5—C4—H4A	120.2	H16B—C16—H16C	109.5
C3—C4—H4A	120.2	O1—S2—O3	113.71 (9)
C4—C5—C6	119.9 (2)	O1—S2—O2	112.89 (9)
C4—C5—H5A	120.0	O3—S2—O2	112.74 (9)
C6—C5—H5A	120.0	O1—S2—C22	106.05 (9)
C1—C6—C5	119.8 (2)	O3—S2—C22	105.82 (9)
C1—C6—C7	119.02 (19)	O2—S2—C22	104.69 (9)
C5—C6—C7	121.1 (2)	C22—C17—C18	119.99 (19)
C8—C7—C6	120.5 (2)	C22—C17—H17A	120.0
C8—C7—H7A	119.8	C18—C17—H17A	120.0
C6—C7—H7A	119.8	C19—C18—C17	118.81 (19)
C7—C8—C9	120.48 (19)	C19—C18—H18A	120.6
C7—C8—H8A	119.8	C17—C18—H18A	120.6
C9—C8—H8A	119.8	C18—C19—C20	122.23 (18)
N1—C9—C8	119.19 (19)	C18—C19—Br1	119.13 (16)
N1—C9—C10	120.16 (19)	C20—C19—Br1	118.64 (15)
C8—C9—C10	120.65 (19)	C19—C20—C21	118.37 (18)
C11—C10—C9	125.4 (2)	C19—C20—H20A	120.8
C11—C10—H10A	117.3	C21—C20—H20A	120.8
C9—C10—H10A	117.3	C20—C21—C22	120.55 (18)
C10—C11—C12	124.4 (2)	C20—C21—H21A	119.7
C10—C11—H11A	117.8	C22—C21—H21A	119.7
C12—C11—H11A	117.8	C17—C22—C21	120.02 (18)
C13—C12—C11	124.9 (2)	C17—C22—S2	121.09 (15)
C13—C12—S1	111.13 (16)	C21—C22—S2	118.77 (15)
C11—C12—S1	123.91 (17)		
C9—N1—C1—C6	2.6 (3)	C9—C10—C11—C12	-179.8 (2)
C16—N1—C1—C6	-177.04 (19)	C10—C11—C12—C13	-178.7 (2)
C9—N1—C1—C2	-176.27 (19)	C10—C11—C12—S1	3.4 (3)
C16—N1—C1—C2	4.1 (3)	C15—S1—C12—C13	0.22 (18)
N1—C1—C2—C3	178.8 (2)	C15—S1—C12—C11	178.3 (2)
C6—C1—C2—C3	0.0 (3)	C11—C12—C13—C14	-178.2 (2)
C1—C2—C3—C4	-0.1 (3)	S1—C12—C13—C14	-0.1 (2)
C2—C3—C4—C5	-0.1 (4)	C12—C13—C14—C15	-0.2 (3)
C3—C4—C5—C6	0.5 (3)	C13—C14—C15—S1	0.3 (3)
N1—C1—C6—C5	-178.50 (18)	C12—S1—C15—C14	-0.3 (2)
C2—C1—C6—C5	0.4 (3)	C22—C17—C18—C19	0.1 (3)
N1—C1—C6—C7	0.4 (3)	C17—C18—C19—C20	-1.6 (3)
C2—C1—C6—C7	179.31 (19)	C17—C18—C19—Br1	178.06 (16)

C4—C5—C6—C1	-0.6 (3)	C18—C19—C20—C21	1.8 (3)
C4—C5—C6—C7	-179.5 (2)	Br1—C19—C20—C21	-177.86 (15)
C1—C6—C7—C8	-2.0 (3)	C19—C20—C21—C22	-0.5 (3)
C5—C6—C7—C8	176.9 (2)	C18—C17—C22—C21	1.2 (3)
C6—C7—C8—C9	0.7 (3)	C18—C17—C22—S2	-174.80 (16)
C1—N1—C9—C8	-3.9 (3)	C20—C21—C22—C17	-1.0 (3)
C16—N1—C9—C8	175.7 (2)	C20—C21—C22—S2	175.11 (15)
C1—N1—C9—C10	176.08 (19)	O1—S2—C22—C17	-9.57 (19)
C16—N1—C9—C10	-4.3 (3)	O3—S2—C22—C17	-130.66 (17)
C7—C8—C9—N1	2.2 (3)	O2—S2—C22—C17	110.03 (17)
C7—C8—C9—C10	-177.8 (2)	O1—S2—C22—C21	174.37 (15)
N1—C9—C10—C11	173.8 (2)	O3—S2—C22—C21	53.28 (18)
C8—C9—C10—C11	-6.2 (3)	O2—S2—C22—C21	-66.04 (17)

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

Cg4 is the centroid of the C17—C22 benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3A $\cdots$ O3 <sup>i</sup>	0.93	2.51	3.409 (3)	162
C7—H7A $\cdots$ O1 <sup>ii</sup>	0.93	2.47	3.241 (3)	140
C8—H8A $\cdots$ O2 <sup>iii</sup>	0.93	2.29	3.218 (3)	175
C10—H10A $\cdots$ S1	0.93	2.77	3.185 (2)	108
C11—H11A $\cdots$ O2 <sup>iii</sup>	0.93	2.31	3.238 (3)	176
C15—H15A $\cdots$ O3 <sup>iv</sup>	0.93	2.40	3.265 (3)	154
C16—H16B $\cdots$ O1 <sup>v</sup>	0.96	2.43	3.321 (3)	155
C17—H17A $\cdots$ O1	0.93	2.54	2.915 (3)	105
C20—H20A $\cdots$ O1 <sup>vi</sup>	0.93	2.32	3.242 (3)	172
C13—H13A $\cdots$ Cg4 <sup>iii</sup>	0.93	2.57	3.434 (2)	155

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

Fig. 1

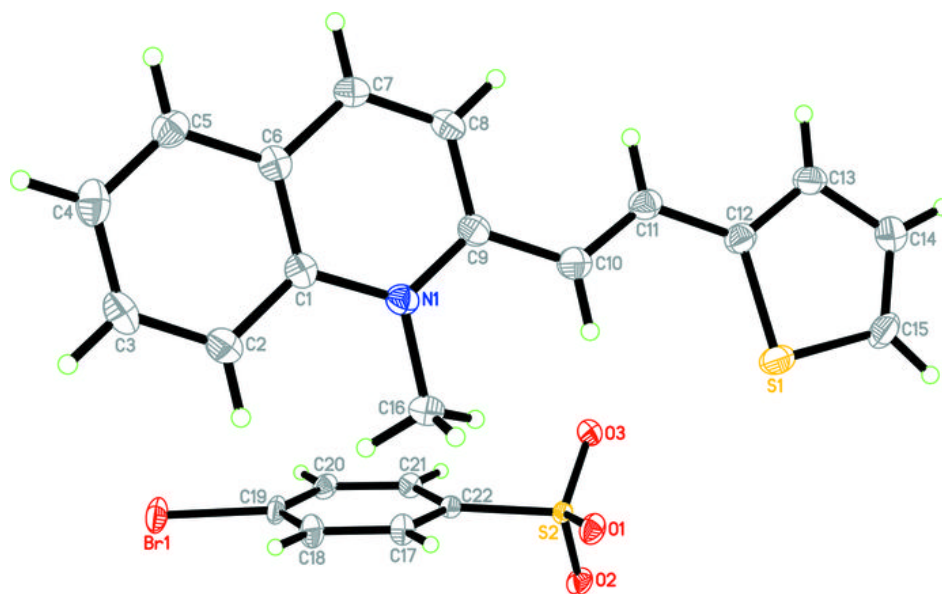


Fig. 2

