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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]-pyridinium 4-chlorobenzenesulfonate¹

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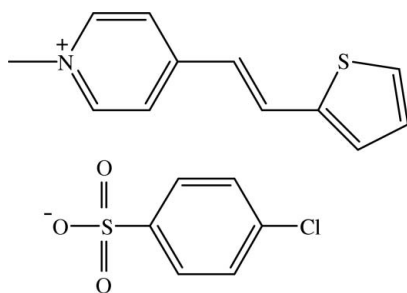
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.038; wR factor = 0.095; data-to-parameter ratio = 20.7.

In the title compound, $\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{ClO}_3\text{S}^-$, the cation is almost planar and exists in the *E* configuration. The cations and anions form alternate layers parallel to the *ab* plane. Within each layer, both cations and anions form chains directed along the *b* axis. The molecules are interconnected by weak $\text{C}-\text{H}\cdots\text{O}$ interactions into a three-dimensional network. The crystal structure is further stabilized by $\text{C}-\text{H}\cdots\pi$ interactions involving the thiophene ring. The sulfonate and thiophene groups are involved in weak intramolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{S}$ interactions, respectively. The latter intramolecular hydrogen bonds produce *S*(5) ring motifs.

Related literature

For bond lengths and angles, see Allen (2002); Allen *et al.* (1987). For related literature on hydrogen-bond motifs, see Bernstein *et al.* (1995). For related structures, see for example Chantrapromma *et al.* (2005, 2006*a,b*, 2007*a,b,c,d*); Drost *et al.* (1995); Jindawong *et al.* (2005); Subramaniyan *et al.* (2003).



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Experimental

Crystal data

$\text{C}_{12}\text{H}_{12}\text{NS}^+\cdot\text{C}_6\text{H}_4\text{ClO}_3\text{S}^-$
 $M_r = 393.91$
 Monoclinic, $P2_1/c$
 $a = 7.3532$ (1) Å
 $b = 14.0250$ (2) Å
 $c = 18.3755$ (2) Å
 $\beta = 111.232$ (1)°
 $V = 1766.41$ (4) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.47$ mm⁻¹
 $T = 100.0$ (1) K
 $0.49 \times 0.22 \times 0.18$ mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.883$, $T_{\max} = 0.919$
 23692 measured reflections
 4688 independent reflections
 3913 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.094$
 $S = 1.06$
 4688 reflections
 227 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.57$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the S1/C8–C11 thiophene ring.

| <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> |
|--------------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C3—H3A···O3 ⁱ | 0.93 | 2.31 | 3.211 (2) | 164 |
| C6—H6A···S1 | 0.93 | 2.84 | 3.228 (2) | 106 |
| C7—H7A···O1 ⁱⁱ | 0.93 | 2.39 | 3.266 (2) | 157 |
| C9—H9A···O3 ⁱⁱⁱ | 0.93 | 2.58 | 3.495 (2) | 166 |
| C10—H10A···O2 ⁱⁱⁱ | 0.93 | 2.39 | 3.302 (2) | 167 |
| C11—H11A···O2 ^{iv} | 0.93 | 2.55 | 3.063 (2) | 115 |
| C12—H12C···O2 ⁱ | 0.96 | 2.39 | 3.334 (2) | 168 |
| C17—H17A···O2 ^{iv} | 0.93 | 2.41 | 3.318 (2) | 166 |
| C18—H18A···O3 | 0.93 | 2.51 | 2.892 (2) | 105 |
| C12—H12B··· <i>Cg</i> 1 ⁱ | 0.96 | 2.69 | 3.515 (2) | 144 |

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

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: SAINT (Bruker, 2005); 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, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2086).

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1-Methyl-4-[(*E*)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

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Comment

Molecules with extended π systems have been extensively used in attempts to obtain materials with non-linear optical (NLO) properties. Organic crystal with the required conjugated π electrons are attractive candidates because of the large NLO coefficients. In our research for second-order NLO materials, we have previously synthesized and crystallized several organic ionic salts of pyridinium and quinolinium derivatives to study their non-linear optical properties (Chantrapromma *et al.*, 2005; 2006a; 2006b; 2007a; 2007b; 2007c; 2007 d; Jindawong *et al.*, 2005). An earlier study carried out by Drost *et al.* (1995) has revealed that the products of the dipole moment and the molecular hyperpolarizability (β) of thiophene-containing conjugated moieties are larger than those of the phenyl analogues. Based on this reason, we have synthesized the title compound which was designed by replacement of the cationic phenyl ring by the thiophene ring that is present in 4-(4'-Hydroxy-3'-methoxystyryl)-1-methylpyridinium 4-chlorobenzenesulfonate (Chantrapromma *et al.*, 2005).

The asymmetric unit of the title compound consists of the $C_{12}H_{12}NS^+$ cation and the $C_6H_4ClO_3S^-$ anion. The cation is almost planar and exists in the *E* configuration with respect to the C6=C7 double bond [1.334 (3) Å]. The cation is almost perpendicular to the anion as is indicated by the angles between the mean planes of the chlorophenyl ring to the pyridinium as well as to the thiophene ring being 87.64 (9)° and 86.73 (9)°, respectively. The dihedral angle between the pyridinium and the thiophene rings is 5.74 (10)°. The ethenyl unit is nearly planar. The torsion angles C4-C5-C6-C7 = -4.3 (3)° and C6-C7-C8-S1 = -1.5 (3)°.

The atom O3 of the sulfonate and the S atom of the thiophene contribute to the C—H \cdots O and C—H \cdots S intramolecular weak interactions (Fig. 1 and Table 1) forming S(5) ring motifs (Bernstein *et al.*, 1995). The bond lengths and angles are normal (Allen *et al.*, 1987) and are comparable with closely related structures (Chantrapromma *et al.*, 2005; 2006b; 2007c; 2007 d).

All the O atoms of 4-chlorobenzenesulfonate anion are involved in the C—H \cdots O weak interactions (Table 1). The cations and anions form alternate layers parallel to the *ab* plane. Within each respective layer, the ions are interconnected by C—H \cdots O weak interactions and in each respective layer can be distinguished chains directed along the *b* axis. The alternating layers are separated by 4.282 (2) Å and are further linked into a three dimensional network by C—H \cdots O weak interactions (Table 1). The sulfonate as well as the thiophene are involved in C—H \cdots O and C—H \cdots S intramolecular weak interactions, respectively. These weak hydrogen bonds participate in S(5) ring motifs. The crystal structure is further stabilized by the C12—H12B $\cdots\pi$ interaction to the thiophene ring C8—C11/S1: C12—H12B=0.96; H12B \cdots Cg1ⁱ=2.692; C12—Cg1ⁱ=3.515 (2) Å; C12—H12B \cdots Cg1ⁱ=144°. [Cg1ⁱ is the centroid of the S1/C8—C11 thiophene ring (symmetry code: (i): 2 - x, 2 - y, 1 - z).]

A very interesting feature is the short non-bonding contact between C11 and O3 that is 2.963 (1) Å long only. A search in the Cambridge Structural Database (version 5.29 and addenda up to 25-th January 2008; Allen, 2002) among the structures which have been flagged with no error or disorder as well as with *R*-factor < 0.05 and which contained chloro-phenyl with

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any substituent in the *para* position showed that the present structure contains an unprecedentedly short contact of this kind. The up-to-now shortest contact of this type was 2.996 (2) Å long and it was observed in MUTDOU [Spiro(2-carbomethoxy-3-(4-chlorophenyl)-5-(*S,R*)-(cis-1-(4-methoxyphenyl) -3-phenyl-4-oxoazetidin-2-(*S,R*)-yl)pyrrolidine-4,3¹-chroman-4¹-one)] determined by Subramaniyan *et al.* (2003).

Experimental

4-(2-Thiophenestyryl)-1-methylpyridinium iodide (compound A) was synthesized by mixing a solution (1:1:1 molar ratio) of 1,4-dimethylpyridinium iodide (2.00 g, 8.5 mmol), 2-thiophenecarboxaldehyde (6.00 ml, 8.5 mmol) and piperidine (0.84 ml, 8.5 mmol) in hot methanol (40 ml). The resulting solution was refluxed for 5 h under a nitrogen atmosphere. The resultant solid was filtered off, washed with diethyl ether and recrystallized from methanol. The title compound was synthesized by mixing compound A (0.10 g, 0.3 mmol) in hot methanol (20 ml) and silver(I) 4-chlorobenzenesulfonate (0.08 g, 0.3 mmol) in hot methanol (30 ml). Silver(I) 4-chlorobenzenesulfonate was synthesized according to our previously reported procedure (Chantrapromma *et al.*, 2006b). The mixture immediately yielded a grey solid of silver iodide. After stirring the mixture for *ca* 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated and a brown solid was obtained. Brown block-shaped single crystals of the title compound suitable for *x*-ray structure determination were recrystallized from methanol solvent by slow evaporation of the solvent at room temperature after several days (Mp. 503–505 K).

Refinement

All the hydrogen atoms could have been discerned in the difference Fourier map. Nevertheless, all the H atoms attached to the carbon atoms were constrained in a riding motion approximation with $C_{\text{aryl}}\text{—H}=0.93$ and $C_{\text{methyl}}\text{—H}=0.968$ Å. The U_{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 Å from C8 and the deepest hole is located at 0.50 Å from S1.

Figures

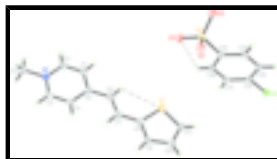


Fig. 1. The title molecules showing 50% probability displacement ellipsoids and the atom-numbering scheme. The intramolecular C—H...O and C—H...S weak interactions are drawn as dashed lines.

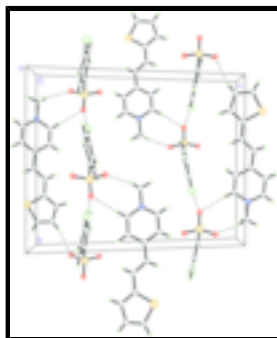


Fig. 2. The packing diagram of the title structure viewed along the *a* axis. The weak C—H...O and C—H...S interactions are drawn as dashed lines.

1-Methyl-4-[(E)-2-(2-thienyl)ethenyl]pyridinium 4-chlorobenzenesulfonate

Crystal data

| | |
|---|---|
| $C_{12}H_{12}NS^+ \cdot C_6H_4ClO_3S^-$ | $F_{000} = 816$ |
| $M_r = 393.91$ | $D_x = 1.481 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Melting point: 503-505 K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation |
| $a = 7.3532 (1) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $b = 14.0250 (2) \text{ \AA}$ | Cell parameters from 4688 reflections |
| $c = 18.3755 (2) \text{ \AA}$ | $\theta = 1.9\text{--}29.0^\circ$ |
| $\beta = 111.232 (1)^\circ$ | $\mu = 0.47 \text{ mm}^{-1}$ |
| $V = 1766.41 (4) \text{ \AA}^3$ | $T = 100.0 (1) \text{ K}$ |
| $Z = 4$ | Block, brown |
| | $0.49 \times 0.22 \times 0.18 \text{ mm}$ |

Data collection

| | |
|--|--|
| Bruker SMART APEX2 CCD area-detector diffractometer | 4688 independent reflections |
| Radiation source: fine-focus sealed tube | 3913 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{\text{int}} = 0.037$ |
| Detector resolution: $8.33 \text{ pixels mm}^{-1}$ | $\theta_{\text{max}} = 29.0^\circ$ |
| $T = 100.0(1) \text{ K}$ | $\theta_{\text{min}} = 1.9^\circ$ |
| ω scans | $h = -10 \rightarrow 10$ |
| Absorption correction: multi-scan (SADABS; Bruker, 2005) | $k = -19 \rightarrow 19$ |
| $T_{\text{min}} = 0.883$, $T_{\text{max}} = 0.919$ | $l = -21 \rightarrow 25$ |
| 23692 measured reflections | |

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | H-atom parameters constrained |
| $wR(F^2) = 0.094$ | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 1.1208P]$ |
| $S = 1.06$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4688 reflections | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 227 parameters | $\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$ |
| 63 constraints | $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$ |
| Primary atom site location: difference Fourier map | Extinction correction: none |

Special details

Experimental. The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.

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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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| S1 | 0.57131 (7) | 0.72654 (3) | 0.43805 (3) | 0.02450 (11) |
| S2 | 1.05267 (5) | 0.60506 (3) | 0.27447 (2) | 0.01477 (10) |
| C11 | 0.37650 (6) | 0.31936 (3) | 0.25045 (2) | 0.02092 (10) |
| O1 | 1.09007 (17) | 0.58763 (9) | 0.20315 (7) | 0.0219 (3) |
| O2 | 1.21870 (16) | 0.58102 (9) | 0.34443 (7) | 0.0196 (3) |
| O3 | 0.97435 (17) | 0.69943 (8) | 0.27824 (7) | 0.0210 (3) |
| N1 | 0.8323 (2) | 1.24164 (11) | 0.49389 (9) | 0.0214 (3) |
| C1 | 0.6981 (3) | 1.10669 (14) | 0.41625 (11) | 0.0273 (4) |
| H1A | 0.6342 | 1.0808 | 0.3669 | 0.033* |
| C2 | 0.7408 (3) | 1.20156 (14) | 0.42351 (11) | 0.0265 (4) |
| H2A | 0.7060 | 1.2394 | 0.3790 | 0.032* |
| C3 | 0.8863 (3) | 1.18711 (14) | 0.55895 (11) | 0.0259 (4) |
| H3A | 0.9501 | 1.2150 | 0.6075 | 0.031* |
| C4 | 0.8481 (3) | 1.09132 (14) | 0.55424 (11) | 0.0267 (4) |
| H4A | 0.8881 | 1.0547 | 0.5995 | 0.032* |
| C5 | 0.7490 (2) | 1.04783 (13) | 0.48184 (11) | 0.0216 (3) |
| C6 | 0.6999 (3) | 0.94698 (14) | 0.47236 (11) | 0.0239 (4) |
| H6A | 0.6262 | 0.9252 | 0.4226 | 0.029* |
| C7 | 0.7537 (3) | 0.88364 (13) | 0.53044 (11) | 0.0227 (4) |
| H7A | 0.8268 | 0.9066 | 0.5799 | 0.027* |
| C8 | 0.7098 (2) | 0.78300 (13) | 0.52426 (10) | 0.0213 (3) |
| C9 | 0.7700 (2) | 0.72058 (12) | 0.58541 (10) | 0.0190 (3) |
| H9A | 0.8451 | 0.7379 | 0.6363 | 0.023* |
| C10 | 0.7037 (3) | 0.62467 (13) | 0.56186 (11) | 0.0234 (4) |
| H10A | 0.7313 | 0.5730 | 0.5958 | 0.028* |
| C11 | 0.5956 (3) | 0.61854 (13) | 0.48386 (11) | 0.0234 (4) |
| H11A | 0.5415 | 0.5622 | 0.4586 | 0.028* |
| C12 | 0.8779 (3) | 1.34470 (13) | 0.50102 (12) | 0.0287 (4) |
| H12A | 0.8119 | 1.3754 | 0.4518 | 0.043* |
| H12B | 1.0161 | 1.3535 | 0.5159 | 0.043* |
| H12C | 0.8353 | 1.3722 | 0.5400 | 0.043* |
| C13 | 0.8648 (2) | 0.52345 (12) | 0.27171 (9) | 0.0151 (3) |
| C14 | 0.8824 (2) | 0.42781 (12) | 0.25482 (9) | 0.0165 (3) |
| H14A | 0.9944 | 0.4067 | 0.2475 | 0.020* |
| C15 | 0.7332 (2) | 0.36386 (12) | 0.24892 (10) | 0.0174 (3) |

| | | | | |
|------|------------|--------------|--------------|------------|
| H15A | 0.7434 | 0.3000 | 0.2372 | 0.021* |
| C16 | 0.5682 (2) | 0.39778 (12) | 0.26093 (9) | 0.0165 (3) |
| C17 | 0.5512 (2) | 0.49151 (12) | 0.28055 (10) | 0.0186 (3) |
| H17A | 0.4417 | 0.5120 | 0.2902 | 0.022* |
| C18 | 0.7013 (2) | 0.55480 (12) | 0.28563 (10) | 0.0181 (3) |
| H18A | 0.6920 | 0.6183 | 0.2984 | 0.022* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|---------------|
| S1 | 0.0255 (2) | 0.0248 (2) | 0.0196 (2) | -0.00284 (17) | 0.00382 (17) | 0.00120 (17) |
| S2 | 0.01233 (18) | 0.01553 (19) | 0.01604 (19) | 0.00021 (14) | 0.00465 (14) | 0.00095 (14) |
| Cl1 | 0.01861 (19) | 0.0189 (2) | 0.0272 (2) | -0.00466 (14) | 0.01069 (16) | -0.00201 (16) |
| O1 | 0.0200 (6) | 0.0292 (7) | 0.0181 (6) | -0.0020 (5) | 0.0090 (5) | 0.0007 (5) |
| O2 | 0.0144 (5) | 0.0239 (6) | 0.0174 (6) | 0.0000 (4) | 0.0022 (5) | 0.0013 (5) |
| O3 | 0.0181 (6) | 0.0143 (6) | 0.0314 (7) | -0.0003 (4) | 0.0099 (5) | 0.0002 (5) |
| N1 | 0.0225 (7) | 0.0214 (7) | 0.0240 (8) | -0.0001 (6) | 0.0127 (6) | 0.0011 (6) |
| C1 | 0.0289 (9) | 0.0304 (10) | 0.0204 (9) | -0.0058 (8) | 0.0063 (7) | -0.0019 (7) |
| C2 | 0.0298 (10) | 0.0285 (10) | 0.0192 (8) | -0.0031 (8) | 0.0066 (7) | 0.0034 (7) |
| C3 | 0.0309 (9) | 0.0293 (10) | 0.0174 (8) | -0.0016 (8) | 0.0085 (7) | -0.0019 (7) |
| C4 | 0.0329 (10) | 0.0273 (10) | 0.0208 (9) | 0.0009 (8) | 0.0108 (8) | 0.0035 (7) |
| C5 | 0.0192 (8) | 0.0227 (9) | 0.0256 (9) | -0.0001 (6) | 0.0114 (7) | -0.0001 (7) |
| C6 | 0.0219 (8) | 0.0285 (9) | 0.0209 (8) | -0.0034 (7) | 0.0073 (7) | -0.0016 (7) |
| C7 | 0.0192 (8) | 0.0274 (9) | 0.0224 (9) | 0.0001 (7) | 0.0086 (7) | -0.0019 (7) |
| C8 | 0.0181 (8) | 0.0239 (9) | 0.0227 (8) | -0.0015 (6) | 0.0085 (7) | -0.0015 (7) |
| C9 | 0.0176 (8) | 0.0251 (9) | 0.0133 (7) | -0.0012 (6) | 0.0045 (6) | 0.0008 (6) |
| C10 | 0.0219 (8) | 0.0249 (9) | 0.0220 (9) | -0.0019 (7) | 0.0061 (7) | 0.0044 (7) |
| C11 | 0.0225 (8) | 0.0211 (9) | 0.0242 (9) | -0.0038 (7) | 0.0058 (7) | 0.0004 (7) |
| C12 | 0.0318 (10) | 0.0219 (9) | 0.0376 (11) | -0.0020 (8) | 0.0186 (9) | -0.0005 (8) |
| C13 | 0.0139 (7) | 0.0171 (8) | 0.0142 (7) | -0.0002 (6) | 0.0048 (6) | -0.0002 (6) |
| C14 | 0.0145 (7) | 0.0190 (8) | 0.0170 (8) | 0.0024 (6) | 0.0068 (6) | -0.0008 (6) |
| C15 | 0.0186 (7) | 0.0148 (7) | 0.0192 (8) | 0.0016 (6) | 0.0075 (6) | -0.0010 (6) |
| C16 | 0.0148 (7) | 0.0176 (8) | 0.0166 (7) | -0.0027 (6) | 0.0051 (6) | 0.0008 (6) |
| C17 | 0.0148 (7) | 0.0180 (8) | 0.0249 (9) | 0.0018 (6) | 0.0094 (7) | 0.0001 (6) |
| C18 | 0.0182 (8) | 0.0148 (8) | 0.0217 (8) | 0.0011 (6) | 0.0078 (6) | -0.0014 (6) |

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

| | | | |
|---------|-------------|----------|-----------|
| S1—C11 | 1.7105 (19) | C7—C8 | 1.443 (3) |
| S1—C8 | 1.7335 (18) | C7—H7A | 0.9300 |
| S2—O1 | 1.4541 (12) | C8—C9 | 1.366 (2) |
| S2—O3 | 1.4550 (12) | C9—C10 | 1.443 (2) |
| S2—O2 | 1.4560 (12) | C9—H9A | 0.9300 |
| S2—C13 | 1.7806 (16) | C10—C11 | 1.367 (3) |
| Cl1—C16 | 1.7428 (16) | C10—H10A | 0.9300 |
| N1—C2 | 1.346 (2) | C11—H11A | 0.9300 |
| N1—C3 | 1.352 (2) | C12—H12A | 0.9600 |
| N1—C12 | 1.479 (2) | C12—H12B | 0.9600 |
| C1—C2 | 1.363 (3) | C12—H12C | 0.9600 |

supplementary materials

| | | | |
|--------------|-------------|---------------|--------------|
| C1—C5 | 1.395 (3) | C13—C18 | 1.388 (2) |
| C1—H1A | 0.9300 | C13—C14 | 1.393 (2) |
| C2—H2A | 0.9300 | C14—C15 | 1.390 (2) |
| C3—C4 | 1.369 (3) | C14—H14A | 0.9300 |
| C3—H3A | 0.9300 | C15—C16 | 1.393 (2) |
| C4—C5 | 1.404 (3) | C15—H15A | 0.9300 |
| C4—H4A | 0.9300 | C16—C17 | 1.381 (2) |
| C5—C6 | 1.455 (3) | C17—C18 | 1.393 (2) |
| C6—C7 | 1.334 (3) | C17—H17A | 0.9300 |
| C6—H6A | 0.9300 | C18—H18A | 0.9300 |
| C11—S1—C8 | 91.87 (9) | C8—C9—C10 | 112.16 (15) |
| O1—S2—O3 | 113.77 (7) | C8—C9—H9A | 123.9 |
| O1—S2—O2 | 112.64 (7) | C10—C9—H9A | 123.9 |
| O3—S2—O2 | 112.86 (7) | C11—C10—C9 | 112.22 (16) |
| O1—S2—C13 | 105.32 (7) | C11—C10—H10A | 123.9 |
| O3—S2—C13 | 105.65 (7) | C9—C10—H10A | 123.9 |
| O2—S2—C13 | 105.68 (7) | C10—C11—S1 | 112.19 (14) |
| C2—N1—C3 | 119.87 (16) | C10—C11—H11A | 123.9 |
| C2—N1—C12 | 120.78 (16) | S1—C11—H11A | 123.9 |
| C3—N1—C12 | 119.34 (16) | N1—C12—H12A | 109.5 |
| C2—C1—C5 | 120.86 (18) | N1—C12—H12B | 109.5 |
| C2—C1—H1A | 119.6 | H12A—C12—H12B | 109.5 |
| C5—C1—H1A | 119.6 | N1—C12—H12C | 109.5 |
| N1—C2—C1 | 121.28 (17) | H12A—C12—H12C | 109.5 |
| N1—C2—H2A | 119.4 | H12B—C12—H12C | 109.5 |
| C1—C2—H2A | 119.4 | C18—C13—C14 | 120.17 (15) |
| N1—C3—C4 | 120.76 (17) | C18—C13—S2 | 120.39 (13) |
| N1—C3—H3A | 119.6 | C14—C13—S2 | 119.44 (12) |
| C4—C3—H3A | 119.6 | C15—C14—C13 | 120.28 (15) |
| C3—C4—C5 | 120.70 (17) | C15—C14—H14A | 119.9 |
| C3—C4—H4A | 119.6 | C13—C14—H14A | 119.9 |
| C5—C4—H4A | 119.6 | C14—C15—C16 | 118.36 (15) |
| C1—C5—C4 | 116.51 (17) | C14—C15—H15A | 120.8 |
| C1—C5—C6 | 119.63 (17) | C16—C15—H15A | 120.8 |
| C4—C5—C6 | 123.86 (17) | C17—C16—C15 | 122.20 (15) |
| C7—C6—C5 | 124.26 (17) | C17—C16—C11 | 118.91 (12) |
| C7—C6—H6A | 117.9 | C15—C16—C11 | 118.89 (13) |
| C5—C6—H6A | 117.9 | C16—C17—C18 | 118.65 (15) |
| C6—C7—C8 | 126.54 (17) | C16—C17—H17A | 120.7 |
| C6—C7—H7A | 116.7 | C18—C17—H17A | 120.7 |
| C8—C7—H7A | 116.7 | C13—C18—C17 | 120.27 (15) |
| C9—C8—C7 | 124.44 (16) | C13—C18—H18A | 119.9 |
| C9—C8—S1 | 111.55 (13) | C17—C18—H18A | 119.9 |
| C7—C8—S1 | 124.01 (14) | | |
| C3—N1—C2—C1 | 1.0 (3) | C8—C9—C10—C11 | -0.1 (2) |
| C12—N1—C2—C1 | 179.98 (18) | C9—C10—C11—S1 | -0.2 (2) |
| C5—C1—C2—N1 | -0.3 (3) | C8—S1—C11—C10 | 0.36 (15) |
| C2—N1—C3—C4 | -0.4 (3) | O1—S2—C13—C18 | -130.91 (14) |

| | | | |
|--------------|--------------|-----------------|--------------|
| C12—N1—C3—C4 | -179.30 (17) | O3—S2—C13—C18 | -10.19 (16) |
| N1—C3—C4—C5 | -1.1 (3) | O2—S2—C13—C18 | 109.65 (14) |
| C2—C1—C5—C4 | -1.0 (3) | O1—S2—C13—C14 | 48.59 (15) |
| C2—C1—C5—C6 | 179.41 (18) | O3—S2—C13—C14 | 169.30 (13) |
| C3—C4—C5—C1 | 1.7 (3) | O2—S2—C13—C14 | -70.85 (14) |
| C3—C4—C5—C6 | -178.76 (17) | C18—C13—C14—C15 | 2.4 (2) |
| C1—C5—C6—C7 | 175.16 (18) | S2—C13—C14—C15 | -177.09 (12) |
| C4—C5—C6—C7 | -4.4 (3) | C13—C14—C15—C16 | -0.5 (2) |
| C5—C6—C7—C8 | -179.72 (17) | C14—C15—C16—C17 | -1.9 (3) |
| C6—C7—C8—C9 | 179.23 (18) | C14—C15—C16—Cl1 | 177.84 (12) |
| C6—C7—C8—S1 | -1.5 (3) | C15—C16—C17—C18 | 2.4 (3) |
| C11—S1—C8—C9 | -0.44 (14) | Cl1—C16—C17—C18 | -177.33 (13) |
| C11—S1—C8—C7 | -179.82 (15) | C14—C13—C18—C17 | -1.9 (2) |
| C7—C8—C9—C10 | 179.78 (16) | S2—C13—C18—C17 | 177.59 (13) |
| S1—C8—C9—C10 | 0.40 (19) | C16—C17—C18—C13 | -0.5 (2) |

Hydrogen-bond geometry (Å, °)

| <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> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C3—H3A...O3 ⁱ | 0.93 | 2.31 | 3.211 (2) | 164 |
| C6—H6A...S1 | 0.93 | 2.84 | 3.228 (2) | 106 |
| C7—H7A...O1 ⁱⁱ | 0.93 | 2.39 | 3.266 (2) | 157 |
| C9—H9A...O3 ⁱⁱ | 0.93 | 2.59 | 3.495 (2) | 166 |
| C10—H10A...O2 ⁱⁱⁱ | 0.93 | 2.39 | 3.302 (2) | 167 |
| C11—H11A...O2 ^{iv} | 0.93 | 2.55 | 3.063 (2) | 115 |
| C12—H12C...O2 ⁱ | 0.96 | 2.39 | 3.334 (2) | 168 |
| C17—H17A...O2 ^{iv} | 0.93 | 2.41 | 3.318 (2) | 166 |
| C18—H18A...O3 | 0.93 | 2.51 | 2.892 (2) | 105 |
| C12—H12B...Cg1 ⁱ | 0.96 | 2.69 | 3.515 (2) | 144 |

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

Fig. 1

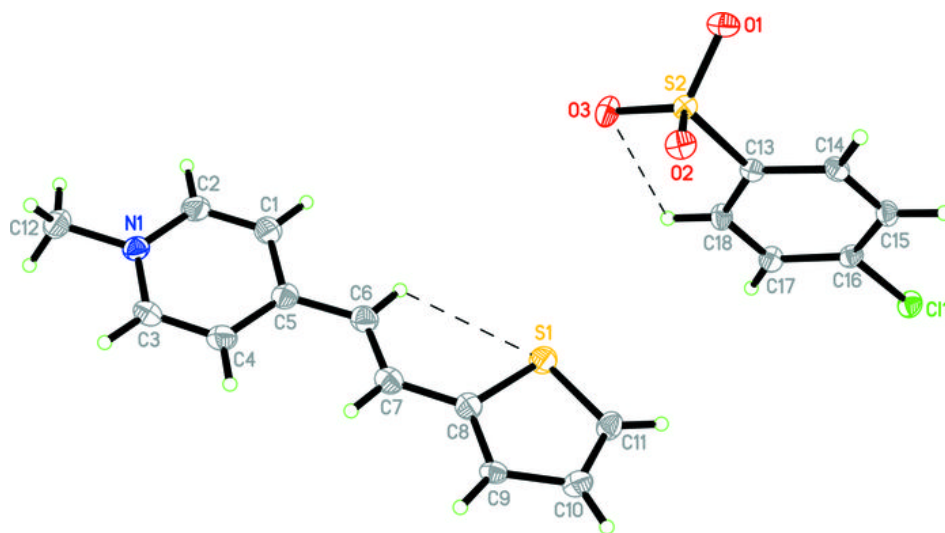


Fig. 2

