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# 1-Methyl-2-[(E)-2-(2-thienyl)ethenyl]-quinolinium iodide<sup>1</sup>

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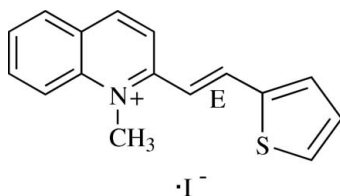
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 Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.023;  $wR$  factor = 0.060; data-to-parameter ratio = 24.6.

In the title compound,  $\text{C}_{16}\text{H}_{14}\text{NS}^+\cdot\text{I}^-$ , the cation has an *E* configuration about the  $\text{C}=\text{C}$  double bond of the ethylene unit. The dihedral angle between the thiophene ring and the quinolinium ring system is  $11.67(11)^\circ$ . A weak  $\text{C}-\text{H}\cdots\text{S}$  intramolecular interaction involving the thiophene ring generates an *S*(5) ring motif. In the crystal structure, the iodide ion, located between the cations arranged in an antiparallel manner, forms weak  $\text{C}-\text{H}\cdots\text{I}$  interactions. The crystal structure is further stabilized by a  $\pi-\pi$  interaction between the thiophene and pyridine rings; the centroid-centroid distance is  $3.6818(13)$  Å.

## Related literature

For bond lengths, see: 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.* (2006, 2008); Chantrapromma, Jindawong & Fun (2007); Chantrapromma, Jindawong, Fun & Patil (2007). For background literature on non-linear optical properties, see, for example: Chou *et al.* (1996); Dittrich *et al.* (2003); Drost *et al.* (1995); Morley (1991).



<sup>1</sup>This paper is dedicated to the late Her Royal Highness Princess Galyani Vadhana Krom Luang Naradhiwas Rajanagarindra for her patronage of science in Thailand.

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## Experimental

### Crystal data

$\text{C}_{16}\text{H}_{14}\text{NS}^+\cdot\text{I}^-$   
 $M_r = 379.25$   
 Triclinic,  $P\bar{1}$   
 $a = 7.8243(1)$  Å  
 $b = 9.6906(1)$  Å  
 $c = 10.7633(2)$  Å  
 $\alpha = 97.521(1)^\circ$   
 $\beta = 95.338(1)^\circ$   
 $\gamma = 112.758(1)^\circ$   
 $V = 736.82(2)$  Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.30$  mm<sup>-1</sup>  
 $T = 100.0(1)$  K  
 $0.58 \times 0.28 \times 0.14$  mm

### Data collection

Bruker SMART APEXII CCD  
 area-detector diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2005)  
 $T_{\min} = 0.346$ ,  $T_{\max} = 0.725$   
 17060 measured reflections  
 4261 independent reflections  
 4118 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.059$   
 $S = 1.10$   
 4261 reflections  
 173 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.50$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.90$  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>
C10—H10A···S1	0.93	2.80	3.189(2)	106
C11—H11A···I1 <sup>i</sup>	0.93	3.06	3.934(2)	157
C16—H16B···I1 <sup>ii</sup>	0.96	3.06	3.962(2)	156

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

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: IS2311).

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## supporting information

*Acta Cryst.* (2008). E64, o1453–o1454 [doi:10.1107/S1600536808020734]

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

Pumsak Ruanwas, Thawanrat Kobkeatthawin, Suchada Chantrapromma, Hoong-Kun Fun and Chatchanok Karalai

### S1. Comment

The design and synthesis of conjugated compounds to search for second-order nonlinear optic (NLO) materials have generated extensive interest. From previous reports, both molecular orbital calculations (Morley, 1991) and experimental studies (Drost *et al.*, 1995) have revealed that the products of dipole moment and molecular hyperpolarizability ( $\nu\beta$ ) of thiophene-containing conjugated moieties are superior to that of benzene analogues. Based on this reason we have previously studied the compound containing thiophene unit, namely, 1-methyl-4-[(*E*)-2-(2-thienyl)ethenyl]-pyridinium 4-chlorobenzenesulfonate (Chantrapromma *et al.*, 2008). In this paper we have synthesized the title compound which was designed by the replacement of the cationic 3-hydroxy-4-methoxyphenyl ring that is present in a compound possessing second-harmonic-generation (SHG) properties, 2-[(*E*)-2-(3-hydroxy-4-methoxyphenyl)ethenyl]-1-methylquinolinium, iodide monohydrate (Chantrapromma, Jindawong, Fun & Patil, 2007) by the thiophene unit. Herein we report the synthesis and crystal structure of the title compound.

The asymmetric unit of the title compound (Fig. 1) consists of the  $C_{16}H_{14}NS^+$  cation and  $I^-$  ion. The cation exists in the *E* configuration with respect to the  $C10=C11$  double bond [1.350 (3) Å] and is almost planar with the interplanar angle between the quinolinium and the thiophene ring being 11.67 (11)° and the torsion angles  $C9-C10-C11-C12 = -178.56$  (17)°. The ethenyl unit is co-planar with the thiophene ring as can be indicated by the torsion angles  $C10-C11-C12-C13 = -179.42$  (18)° and  $C10-C11-C12-S1 = 1.4$  (3)°. It is slightly deviated from the quinolinium ring with the torsion angle  $C8-C9-C10-C11 = -14.2$  (3)°. The atom S1 of the thiophene ring contributes to the  $C-H\cdots S$  intramolecular weak interaction (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.*, 2006, 2008; Chantrapromma, Jindawong & Fun, 2007; Chantrapromma, Jindawong, Fun & Patil, 2007).

In the crystal packing (Fig. 2), the  $I^-$  ion is in between each pair of the two antiparallel cations and is linked with the cations through weak  $C-H\cdots I$  interactions. The crystal is stabilized by weak  $C-H\cdots S$  and  $C-H\cdots I$  interactions (Table 1). A  $\pi-\pi$  interaction was observed with the  $Cg_1\cdots Cg_2$  distance of 3.6818 (13) Å;  $Cg_1^i$  and  $Cg_2^i$  are the centroids of the  $S1/C12-C15$  and  $N1/C1/C6-C9$  rings, respectively [symmetry code: (i): 1 - *x*, 1 - *y*, 1 - *z*]. The perpendicular distances of  $Cg_2$  onto the plane of the  $S1/C12-C15$  ring and  $Cg_1$  onto the plane of the  $N1/C1/C6-C9$  ring are 3.200 and 3.500 Å, respectively

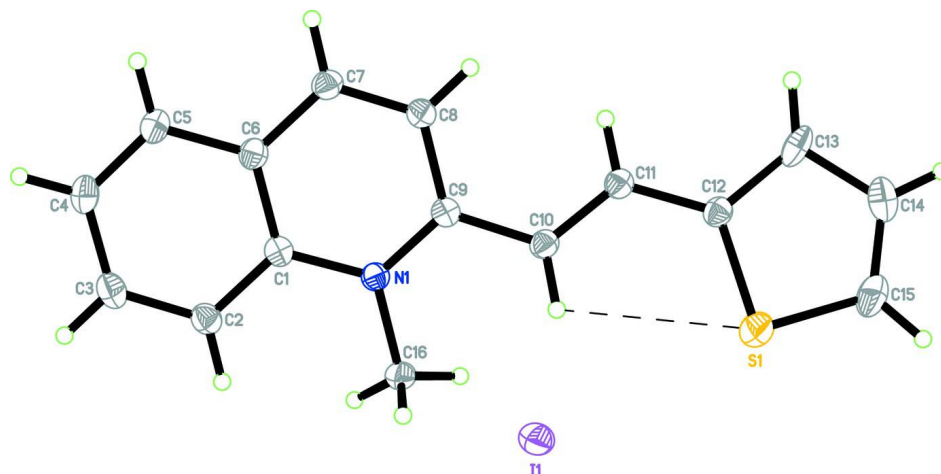
### S2. Experimental

2-(2-Thiophenestyryl)-1-methylquinolinium iodide 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 hr under a nitrogen atmosphere. The resultant solid was filtered off and washed with diethyl ether. Brown block-shaped single crystals of the title compound

suitable for *x*-ray structure determination were obtained after recrystallization from methanol by slow evaporation of the solvent at room temperature after a few weeks.

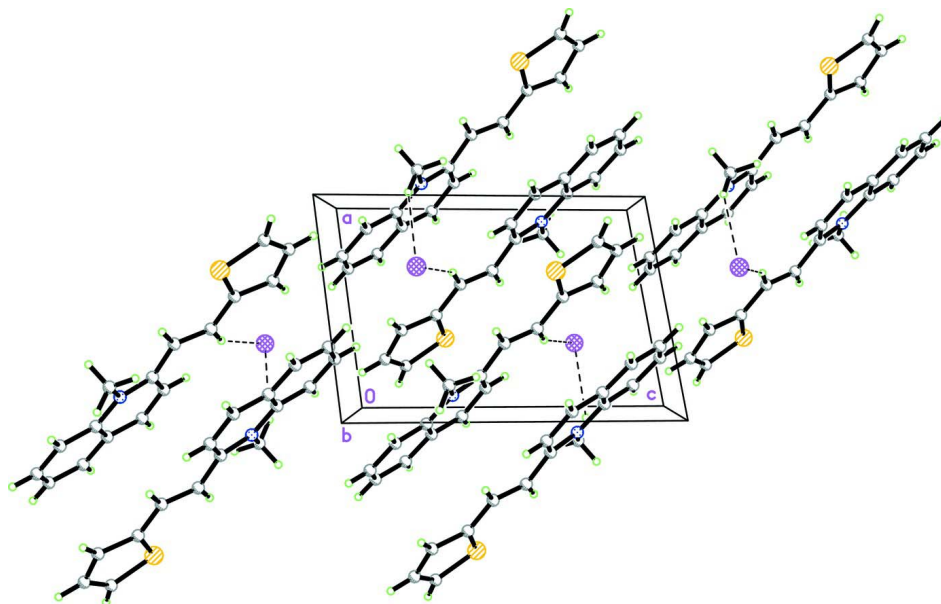
### S3. Refinement

All H atoms were placed in calculated positions ( $C-H = 0.93-0.96 \text{ \AA}$ ) and were refined as riding, with  $U_{iso}(H) = 1.2U_{eq}(C)$  or  $1.5U_{eq}(\text{methyl } C)$ . A rotating group model was used for the methyl group. The highest residual electron density peak is located at  $0.75 \text{ \AA}$  from atom I1 and the deepest hole is located at  $0.38 \text{ \AA}$  from atom S1.



**Figure 1**

The title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. The weak  $C-H \cdots S$  intramolecular interaction was drawn as a dashed line.



**Figure 2**

The packing diagram of the title structure, viewed approximately along the *b* axis. Weak  $C-H \cdots I$  interactions were drawn as dashed lines.

## 1-Methyl-2-[(E)-2-(2-thienyl)ethenyl]quinolinium iodide

## Crystal data

C<sub>16</sub>H<sub>14</sub>NS<sup>+</sup>·I<sup>-</sup> $M_r = 379.25$ Triclinic,  $P\bar{1}$ 

Hall symbol: -P 1

 $a = 7.8243$  (1) Å $b = 9.6906$  (1) Å $c = 10.7633$  (2) Å $\alpha = 97.521$  (1)° $\beta = 95.338$  (1)° $\gamma = 112.758$  (1)° $V = 736.82$  (2) Å<sup>3</sup> $Z = 2$  $F(000) = 372$  $D_x = 1.709$  Mg m<sup>-3</sup>Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4261 reflections

 $\theta = 2.3$ – $30.0$ ° $\mu = 2.30$  mm<sup>-1</sup> $T = 100$  K

Block, brown

 $0.58 \times 0.28 \times 0.14$  mm

## Data collection

Bruker SMART APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.33 pixels mm<sup>-1</sup> $\omega$  scansAbsorption correction: multi-scan  
(SADABS; Bruker, 2005) $T_{\min} = 0.346$ ,  $T_{\max} = 0.725$ 

17060 measured reflections

4261 independent reflections

4118 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.018$  $\theta_{\max} = 30.0$ °,  $\theta_{\min} = 2.3$ ° $h = -11 \rightarrow 11$  $k = -13 \rightarrow 13$  $l = -15 \rightarrow 15$ 

## Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.022$  $wR(F^2) = 0.059$  $S = 1.10$ 

4261 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
mapHydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.8519P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.002$  $\Delta\rho_{\max} = 1.50$  e Å<sup>-3</sup> $\Delta\rho_{\min} = -0.90$  e Å<sup>-3</sup>

## Special details

**Experimental.** The low-temperature data was collected with the Oxford Cryosystem Cobra low-temperature attachment.**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<sup>2</sup>)

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.681003 (17)	0.790360 (14)	0.269777 (12)	0.02186 (5)
S1	0.65928 (8)	0.89200 (6)	0.69144 (6)	0.02828 (11)

N1	0.0896 (2)	0.54762 (17)	0.31586 (15)	0.0162 (3)
C1	-0.0473 (3)	0.4405 (2)	0.21950 (17)	0.0167 (3)
C2	-0.1289 (3)	0.4838 (2)	0.11749 (18)	0.0198 (3)
H2A	-0.0945	0.5863	0.1138	0.024*
C3	-0.2600 (3)	0.3734 (2)	0.02336 (19)	0.0227 (4)
H3A	-0.3128	0.4025	-0.0441	0.027*
C4	-0.3158 (3)	0.2180 (2)	0.02687 (19)	0.0227 (4)
H4A	-0.4034	0.1452	-0.0382	0.027*
C5	-0.2405 (3)	0.1739 (2)	0.12667 (19)	0.0206 (3)
H5A	-0.2781	0.0711	0.1297	0.025*
C6	-0.1062 (3)	0.2843 (2)	0.22486 (18)	0.0180 (3)
C7	-0.0267 (3)	0.2412 (2)	0.32868 (18)	0.0193 (3)
H7A	-0.0686	0.1391	0.3357	0.023*
C8	0.1112 (3)	0.3491 (2)	0.41844 (18)	0.0180 (3)
H8A	0.1644	0.3198	0.4855	0.022*
C9	0.1745 (2)	0.5058 (2)	0.41052 (17)	0.0161 (3)
C10	0.3282 (3)	0.6203 (2)	0.50081 (18)	0.0175 (3)
H10A	0.3838	0.7174	0.4822	0.021*
C11	0.3950 (3)	0.5929 (2)	0.61089 (17)	0.0174 (3)
H11A	0.3399	0.4946	0.6273	0.021*
C12	0.5444 (3)	0.7036 (2)	0.70463 (18)	0.0177 (3)
C13	0.6158 (3)	0.6721 (2)	0.82202 (19)	0.0217 (4)
H13A	0.5752	0.5776	0.8468	0.026*
C14	0.7577 (3)	0.8091 (3)	0.8930 (2)	0.0282 (4)
H14A	0.8203	0.8145	0.9724	0.034*
C15	0.7946 (3)	0.9321 (3)	0.8350 (2)	0.0300 (4)
H15A	0.8850	1.0285	0.8706	0.036*
C16	0.1413 (3)	0.7112 (2)	0.31385 (19)	0.0211 (3)
H16A	0.1810	0.7677	0.3991	0.032*
H16B	0.0345	0.7250	0.2756	0.032*
H16C	0.2418	0.7471	0.2655	0.032*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
II	0.02044 (7)	0.02041 (7)	0.02481 (7)	0.00758 (5)	0.00089 (5)	0.00842 (5)
S1	0.0287 (3)	0.0207 (2)	0.0312 (3)	0.00775 (19)	-0.0017 (2)	0.00210 (19)
N1	0.0151 (7)	0.0161 (7)	0.0176 (7)	0.0066 (5)	0.0021 (5)	0.0033 (5)
C1	0.0158 (7)	0.0191 (8)	0.0165 (8)	0.0083 (6)	0.0035 (6)	0.0031 (6)
C2	0.0179 (8)	0.0227 (9)	0.0192 (8)	0.0082 (7)	0.0029 (6)	0.0058 (7)
C3	0.0202 (8)	0.0295 (10)	0.0184 (8)	0.0101 (7)	0.0013 (7)	0.0056 (7)
C4	0.0178 (8)	0.0262 (9)	0.0197 (8)	0.0065 (7)	-0.0009 (7)	-0.0006 (7)
C5	0.0188 (8)	0.0193 (8)	0.0213 (8)	0.0068 (7)	0.0007 (7)	-0.0005 (7)
C6	0.0161 (8)	0.0187 (8)	0.0184 (8)	0.0068 (6)	0.0023 (6)	0.0019 (6)
C7	0.0195 (8)	0.0165 (8)	0.0217 (8)	0.0075 (7)	0.0028 (7)	0.0028 (6)
C8	0.0183 (8)	0.0177 (8)	0.0181 (8)	0.0077 (6)	0.0017 (6)	0.0033 (6)
C9	0.0153 (7)	0.0175 (8)	0.0164 (7)	0.0074 (6)	0.0036 (6)	0.0030 (6)
C10	0.0178 (8)	0.0154 (7)	0.0188 (8)	0.0064 (6)	0.0023 (6)	0.0021 (6)

C11	0.0158 (8)	0.0173 (8)	0.0190 (8)	0.0070 (6)	0.0026 (6)	0.0023 (6)
C12	0.0168 (8)	0.0163 (8)	0.0198 (8)	0.0069 (6)	0.0026 (6)	0.0015 (6)
C13	0.0121 (7)	0.0217 (9)	0.0238 (9)	0.0014 (6)	0.0068 (6)	-0.0071 (7)
C14	0.0231 (9)	0.0395 (12)	0.0201 (9)	0.0132 (9)	-0.0010 (7)	0.0002 (8)
C15	0.0263 (10)	0.0248 (10)	0.0295 (11)	0.0056 (8)	-0.0030 (8)	-0.0066 (8)
C16	0.0219 (9)	0.0163 (8)	0.0245 (9)	0.0075 (7)	-0.0003 (7)	0.0051 (7)

*Geometric parameters (Å, °)*

S1—C15	1.697 (2)	C7—H7A	0.9300
S1—C12	1.7273 (19)	C8—C9	1.421 (2)
N1—C9	1.354 (2)	C8—H8A	0.9300
N1—C1	1.397 (2)	C9—C10	1.446 (3)
N1—C16	1.481 (2)	C10—C11	1.350 (3)
C1—C2	1.410 (3)	C10—H10A	0.9300
C1—C6	1.413 (3)	C11—C12	1.436 (3)
C2—C3	1.377 (3)	C11—H11A	0.9300
C2—H2A	0.9300	C12—C13	1.450 (3)
C3—C4	1.403 (3)	C13—C14	1.420 (3)
C3—H3A	0.9300	C13—H13A	0.9300
C4—C5	1.371 (3)	C14—C15	1.361 (4)
C4—H4A	0.9300	C14—H14A	0.9300
C5—C6	1.412 (3)	C15—H15A	0.9300
C5—H5A	0.9300	C16—H16A	0.9600
C6—C7	1.415 (3)	C16—H16B	0.9600
C7—C8	1.364 (3)	C16—H16C	0.9600
C15—S1—C12	91.58 (11)	N1—C9—C8	119.08 (16)
C9—N1—C1	121.89 (16)	N1—C9—C10	119.79 (16)
C9—N1—C16	119.57 (16)	C8—C9—C10	121.13 (17)
C1—N1—C16	118.53 (15)	C11—C10—C9	123.13 (17)
N1—C1—C2	121.92 (17)	C11—C10—H10A	118.4
N1—C1—C6	118.98 (16)	C9—C10—H10A	118.4
C2—C1—C6	119.09 (17)	C10—C11—C12	125.11 (17)
C3—C2—C1	119.54 (18)	C10—C11—H11A	117.4
C3—C2—H2A	120.2	C12—C11—H11A	117.4
C1—C2—H2A	120.2	C11—C12—C13	124.49 (17)
C2—C3—C4	121.53 (19)	C11—C12—S1	123.74 (15)
C2—C3—H3A	119.2	C13—C12—S1	111.77 (14)
C4—C3—H3A	119.2	C14—C13—C12	108.83 (19)
C5—C4—C3	119.69 (18)	C14—C13—H13A	125.6
C5—C4—H4A	120.2	C12—C13—H13A	125.6
C3—C4—H4A	120.2	C15—C14—C13	114.4 (2)
C4—C5—C6	120.20 (18)	C15—C14—H14A	122.8
C4—C5—H5A	119.9	C13—C14—H14A	122.8
C6—C5—H5A	119.9	C14—C15—S1	113.38 (17)
C5—C6—C1	119.91 (18)	C14—C15—H15A	123.3
C5—C6—C7	121.09 (17)	S1—C15—H15A	123.3

C1—C6—C7	118.99 (17)	N1—C16—H16A	109.5
C8—C7—C6	120.12 (17)	N1—C16—H16B	109.5
C8—C7—H7A	119.9	H16A—C16—H16B	109.5
C6—C7—H7A	119.9	N1—C16—H16C	109.5
C7—C8—C9	120.69 (18)	H16A—C16—H16C	109.5
C7—C8—H8A	119.7	H16B—C16—H16C	109.5
C9—C8—H8A	119.7		
C9—N1—C1—C2	-176.75 (17)	C1—N1—C9—C8	-5.6 (3)
C16—N1—C1—C2	3.6 (3)	C16—N1—C9—C8	173.99 (16)
C9—N1—C1—C6	3.5 (3)	C1—N1—C9—C10	173.83 (16)
C16—N1—C1—C6	-176.05 (16)	C16—N1—C9—C10	-6.6 (2)
N1—C1—C2—C3	178.41 (17)	C7—C8—C9—N1	3.2 (3)
C6—C1—C2—C3	-1.9 (3)	C7—C8—C9—C10	-176.23 (17)
C1—C2—C3—C4	0.5 (3)	N1—C9—C10—C11	166.39 (17)
C2—C3—C4—C5	0.8 (3)	C8—C9—C10—C11	-14.2 (3)
C3—C4—C5—C6	-0.6 (3)	C9—C10—C11—C12	-178.56 (17)
C4—C5—C6—C1	-0.8 (3)	C10—C11—C12—C13	-179.42 (18)
C4—C5—C6—C7	-179.96 (18)	C10—C11—C12—S1	1.4 (3)
N1—C1—C6—C5	-178.25 (16)	C15—S1—C12—C11	178.33 (17)
C2—C1—C6—C5	2.0 (3)	C15—S1—C12—C13	-0.98 (15)
N1—C1—C6—C7	0.9 (3)	C11—C12—C13—C14	-177.85 (18)
C2—C1—C6—C7	-178.77 (17)	S1—C12—C13—C14	1.5 (2)
C5—C6—C7—C8	175.96 (18)	C12—C13—C14—C15	-1.3 (3)
C1—C6—C7—C8	-3.2 (3)	C13—C14—C15—S1	0.6 (3)
C6—C7—C8—C9	1.2 (3)	C12—S1—C15—C14	0.22 (19)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C10—H10A $\cdots$ S1	0.93	2.80	3.189 (2)	106
C11—H11A $\cdots$ I1 <sup>i</sup>	0.93	3.06	3.934 (2)	157
C16—H16B $\cdots$ I1 <sup>ii</sup>	0.96	3.06	3.962 (2)	156

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