

# (*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methylbenzenesulfonate monohydrate<sup>1</sup>

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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.072;  $wR$  factor = 0.203; data-to-parameter ratio = 17.3.

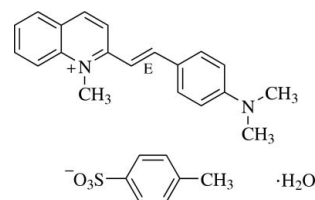
In the title compound,  $\text{C}_{20}\text{H}_{21}\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^- \cdot \text{H}_2\text{O}$ , the cation is essentially planar, as indicated by the dihedral angle of  $2.79$  ( $13$ )° between the quinolinium and the dimethylamino-phenyl rings, and exists in the *E* configuration. The  $\pi$ -conjugated planes of the cation and the anion are inclined to each other at a dihedral angle of  $66.95$  ( $12$ )°. The cation is linked to the anion through  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds and the anion is further linked with the water molecule by  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds, forming a three-molecule unit. These units are arranged in a face-to-face manner into a ribbon-like structure along the *b* axis. The ribbons are stacked along the *c* axis. The crystal structure is further stabilized by  $\text{C}-\text{H} \cdots \pi$  interactions involving the dimethylaminophenyl and methylphenyl rings. A  $\pi$ - $\pi$  interaction with a centroid-centroid distance of  $3.6074$  ( $19$ ) Å is also observed.

## Related literature

For bond-length data, see: Allen *et al.* (1987). For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995). For background to NLO materials research, see: Dittrich *et al.* (2003); Nogi *et al.* (2000); Ogawa *et al.* (2008); Otero *et al.* (2002); Sato *et al.* (1999); Weir *et al.* (2003); Yang *et al.* (2007). For related structures, see, for example: Adachi *et al.* (1999); Chantrapromma *et al.* (2008); Ogawa *et al.* (2008); Rahman *et al.* (2003).

<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

$\text{C}_{20}\text{H}_{21}\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^- \cdot \text{H}_2\text{O}$

$M_r = 478.60$

Triclinic,  $P\bar{1}$

$a = 10.9739$  (5) Å

$b = 11.1789$  (5) Å

$c = 11.1923$  (9) Å

$\alpha = 97.133$  (5)°

$\beta = 100.322$  (5)°

$\gamma = 117.021$  (3)°

$V = 1169.78$  (13) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 0.18$  mm<sup>-1</sup>

$T = 100.0$  (1) K

$0.24 \times 0.19 \times 0.08$  mm

### Data collection

Bruker SMART APEX2 CCD area-

detector diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.958$ ,  $T_{\max} = 0.986$

17557 measured reflections

5390 independent reflections

3272 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.073$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.072$

$wR(F^2) = 0.203$

$S = 1.05$

5390 reflections

311 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.60$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.47$  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> |
|--------------------------------|---------------------|---------------------|---------------------|--------------------------------|
| O1W—H1W⋯O2                     | 0.90                | 1.96                | 2.839 (4)           | 164                            |
| O1W—H2W⋯O1 <sup>i</sup>        | 0.88                | 2.01                | 2.893 (3)           | 179                            |
| C10—H10A⋯O3 <sup>ii</sup>      | 0.93                | 2.57                | 3.460 (4)           | 162                            |
| C17—H17A⋯O3 <sup>ii</sup>      | 0.93                | 2.45                | 3.344 (5)           | 163                            |
| C20—H20A⋯O3 <sup>ii</sup>      | 0.96                | 2.33                | 3.204 (6)           | 151                            |
| C20—H20B⋯O1 <sup>iii</sup>     | 0.96                | 2.49                | 3.388 (4)           | 156                            |
| C26—H26A⋯O2                    | 0.93                | 2.51                | 2.884 (5)           | 104                            |
| C7—H7A⋯Cg4 <sup>iv</sup>       | 0.93                | 2.97                | 3.615 (4)           | 128                            |
| C23—H23A⋯Cg3 <sup>v</sup>      | 0.93                | 2.82                | 3.594 (4)           | 141                            |

Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $-x + 1, -y, -z + 1$ ; (v)  $-x + 1, -y, -z$ . Cg3 and Cg4 are the centroids of the C12—C17 and C21—C26 rings, respectively.

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, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2369).

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**supplementary materials**

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**(*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methylbenzenesulfonate monohydrate**

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

**Comment**

There has been considerable interest in organic nonlinear optical materials that could be used for applications including telecommunications, optical computing and optical data storage. Organic crystals with extensive conjugated  $\pi$  systems are attractive candidates for nonlinear optic (NLO) studies because of their large hyperpolarizability ( $\beta$ ) and ease of preparation (Dittrich *et al.*, 2003; Nogi *et al.*, 2000; Ogawa *et al.*, 2008; Otero *et al.*, 2002; Sato *et al.*, 1999; Weir *et al.*, 2003; Yang *et al.*, 2007). 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium tosylate (DAST) is one of the promising NLO material (Adachi *et al.*, 1999). Previous studies (Dittrich *et al.*, 2003; Nogi *et al.*, 2000; Sato *et al.*, 1999) have shown that the DAST and its analogues exhibit second-order non-linear optical properties. One strategy to enhance the hyperpolarizability of the cations is by elongation of its  $\pi$ -conjugation system. Based on these previous studies, we have synthesized the title compound which was designed by increasing the  $\pi$ -conjugate system with the replacement of the cationic pyridinium ring that is present in DAST by the quinolinium ring. The crystal structure of the title compound is reported in this study.

Figure 1 shows the asymmetric unit of the title compound (I) which consists of a  $C_{20}H_{21}N_2^+$  cation, a  $C_7H_7O_3S^-$  anion and one  $H_2O$  molecule. The cation exists in the *E* configuration with respect to the C10=C11 double bond [1.328 (4) Å, the corresponding value is 1.357 (2) Å in Chantrapromma *et al.*, 2008]. The cation molecule is essentially planar as indicated by the dihedral angle between the quinolinium and the dimethylaminophenyl rings being 2.79 (13)° [9.26 (6)° in Chantrapromma *et al.*, 2008] with the torsion angles C8–C9–C10–C11 = -0.1 (5)° and C10–C11–C12–C17 = 2.4 (5)°. Both methyl groups of dimethylamino moiety are slightly twisted from the mean plane of the attached C12–C17 ring as indicated by the torsion angle C18–N2–C15–C14 = 3.6 (4)° and C19–N2–C15–C16 = -6.3 (4)°. The relative arrangement of cation and anion is shown by the interplanar angles between the mean plane of the 4-methylphenyl ring and those of the quinolinium and dimethylaminophenyl system which are 67.80 (13) and 67.19 (16)°, respectively. Besides the O—H $\cdots$ O hydrogen bonded to water molecule, the atom O2 of the sulfonate also contributed to a weak intramolecular C26—H26A $\cdots$ O2 interaction (Table 1) forming an S(5) ring motif (Bernstein *et al.*, 1995). The bond lengths (Allen *et al.*, 1987) and angles in (I) are in normal ranges and comparable with a related structure (Chantrapromma *et al.*, 2008).

In the crystal packing, all O atoms of the sulfonate group are involved in weak C—H $\cdots$ O interactions (Table 1). The cation is linked to the anion by weak C—H $\cdots$ O interactions and the anion is further linked to the water molecule by O—H $\cdots$ O hydrogen bonds, forming a three-molecule unit (Table 1 and Fig. 2). These three-molecule units are arranged in a face-to-face manner into a ribbon-like structure along the *b* axis and these ribbons are stacked along the *c* axis (Fig. 2). The crystal structure is further stabilized by C—H $\cdots$  $\pi$  interactions (Table 1). A  $\pi$ - $\pi$  interaction with the distance  $Cg_1\cdots Cg_2^{iv} = 3.6074$  (19) Å [symmetry code: (iv) 1 - *x*, -*y*, 1 - *z*] is observed;  $Cg_1$ ,  $Cg_2$ ,  $Cg_3$  and  $Cg_4$  are the centroids of the N1/C1/C6–C9, C1–C6, C12–C17 and C21–C26 rings, respectively.

## Experimental

(*E*)-2-[4-(Dimethylamino)styryl]-1-methylpyridinium iodide (compound A) was synthesized according to our previously reported procedure (Chantrapromma *et al.*, 2008). Silver(I) *p*-toluenesulfonate (compound B) was synthesized according to a previous method (Rahman *et al.*, 2003). The title compound was then prepared by mixing compound A (0.20 g, 0.5 mmol) in hot methanol (50 ml) and compound B (0.12 g, 0.5 mmol) in hot methanol (30 ml). The mixture immediately yielded a grey precipitate of silver iodide. After stirring the mixture for 30 min, the precipitate of silver iodide was removed and the resulting solution was evaporated yielding a green solid. Green 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 a few weeks (m.p. 557–558 K).

## Refinement

All H atoms were placed in calculated positions, with  $d(\text{O—H}) = 0.88\text{--}0.90 \text{ \AA}$ ,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ ,  $d(\text{C—H}) = 0.93 \text{ \AA}$ ,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic and CH, and  $0.96 \text{ \AA}$ ,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for  $\text{CH}_3$  atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at  $0.98 \text{ \AA}$  from C8 and the deepest hole is located at  $0.96 \text{ \AA}$  from S1.

## Figures

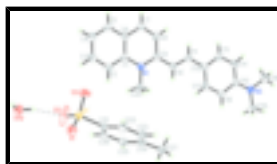


Fig. 1. The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

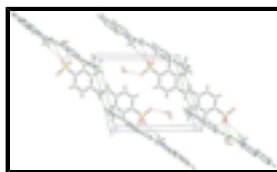


Fig. 2. The crystal packing of (I) viewed along the *b* axis. The O—H...O and weak C—H...O interactions are drawn as dashed lines.

## (*E*)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methylbenzenesulfonate monohydrate

### Crystal data

$\text{C}_{20}\text{H}_{21}\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^- \cdot \text{H}_2\text{O}$

$M_r = 478.60$

Triclinic, *P* $\bar{1}$

Hall symbol: -P 1

$a = 10.9739 (5) \text{ \AA}$

$b = 11.1789 (5) \text{ \AA}$

$c = 11.1923 (9) \text{ \AA}$

$\alpha = 97.133 (5)^\circ$

$Z = 2$

$F_{000} = 508$

$D_x = 1.359 \text{ Mg m}^{-3}$

Melting point = 557–558 K

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5390 reflections

$\theta = 1.2\text{--}27.5^\circ$

$\mu = 0.18 \text{ mm}^{-1}$

$\beta = 100.322 (5)^\circ$   
 $\gamma = 117.021 (3)^\circ$   
 $V = 1169.78 (13) \text{ \AA}^3$

$T = 100.0 (1) \text{ K}$   
 Block, green  
 $0.24 \times 0.19 \times 0.08 \text{ mm}$

*Data collection*

Bruker SMART APEX2 CCD area-detector diffractometer  
 Radiation source: fine-focus sealed tube  
 Monochromator: graphite  
 Detector resolution: 8.33 pixels  $\text{mm}^{-1}$   
 $T = 100.0(1) \text{ K}$   
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2005)  
 $T_{\min} = 0.958, T_{\max} = 0.986$   
 17557 measured reflections

5390 independent reflections  
 3272 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.073$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $\theta_{\text{min}} = 1.9^\circ$   
 $h = -14 \rightarrow 14$   
 $k = -14 \rightarrow 14$   
 $l = -14 \rightarrow 11$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.072$   
 $wR(F^2) = 0.203$   
 $S = 1.05$   
 5390 reflections  
 311 parameters  
 Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map  
 Hydrogen site location: inferred from neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 0.1631P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$   
 Extinction correction: none

*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 ( $\text{Å}^2$ )*

x y z  $U_{\text{iso}}^*/U_{\text{eq}}$

## supplementary materials

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|      |             |             |             |             |
|------|-------------|-------------|-------------|-------------|
| S1   | 0.16105 (8) | 0.41169 (9) | 0.37784 (7) | 0.0306 (2)  |
| O1   | 0.0863 (2)  | 0.4772 (2)  | 0.3214 (2)  | 0.0361 (6)  |
| O2   | 0.2576 (3)  | 0.4944 (4)  | 0.4973 (2)  | 0.0784 (11) |
| O3   | 0.0690 (3)  | 0.2712 (3)  | 0.3786 (3)  | 0.0708 (10) |
| O1W  | 0.2135 (2)  | 0.6205 (2)  | 0.7095 (2)  | 0.0371 (6)  |
| H1W  | 0.2122      | 0.5660      | 0.6424      | 0.056*      |
| H2W  | 0.1227      | 0.5918      | 0.7009      | 0.056*      |
| N1   | 0.7361 (3)  | 0.0767 (3)  | 0.5500 (2)  | 0.0286 (6)  |
| N2   | 1.1460 (3)  | -0.1954 (3) | 0.0336 (2)  | 0.0342 (6)  |
| C1   | 0.6510 (3)  | 0.0789 (3)  | 0.6300 (3)  | 0.0270 (7)  |
| C2   | 0.6415 (3)  | 0.1968 (3)  | 0.6702 (3)  | 0.0331 (7)  |
| H2A  | 0.6928      | 0.2775      | 0.6453      | 0.040*      |
| C3   | 0.5566 (3)  | 0.1928 (3)  | 0.7459 (3)  | 0.0343 (8)  |
| H3A  | 0.5517      | 0.2722      | 0.7728      | 0.041*      |
| C4   | 0.4776 (3)  | 0.0760 (4)  | 0.7845 (3)  | 0.0335 (8)  |
| H4A  | 0.4200      | 0.0770      | 0.8359      | 0.040*      |
| C5   | 0.4840 (3)  | -0.0424 (3) | 0.7467 (3)  | 0.0332 (8)  |
| H5A  | 0.4311      | -0.1218     | 0.7726      | 0.040*      |
| C6   | 0.5721 (3)  | -0.0429 (3) | 0.6678 (3)  | 0.0283 (7)  |
| C7   | 0.5835 (3)  | -0.1616 (3) | 0.6271 (3)  | 0.0333 (7)  |
| H7A  | 0.5333      | -0.2419     | 0.6529      | 0.040*      |
| C8   | 0.6659 (3)  | -0.1590 (3) | 0.5517 (3)  | 0.0321 (7)  |
| H8A  | 0.6733      | -0.2375     | 0.5274      | 0.039*      |
| C9   | 0.7441 (3)  | -0.0373 (3) | 0.5067 (3)  | 0.0252 (6)  |
| C10  | 0.8232 (3)  | -0.0412 (3) | 0.4199 (3)  | 0.0281 (7)  |
| H10A | 0.8713      | 0.0395      | 0.3939      | 0.034*      |
| C11  | 0.8347 (3)  | -0.1494 (3) | 0.3726 (3)  | 0.0310 (7)  |
| H11A | 0.7869      | -0.2295     | 0.3996      | 0.037*      |
| C12  | 0.9139 (3)  | -0.1564 (3) | 0.2832 (3)  | 0.0297 (7)  |
| C13  | 0.9132 (3)  | -0.2798 (3) | 0.2436 (3)  | 0.0335 (7)  |
| H13A | 0.8599      | -0.3560     | 0.2733      | 0.040*      |
| C14  | 0.9879 (3)  | -0.2927 (3) | 0.1630 (3)  | 0.0304 (7)  |
| H14A | 0.9845      | -0.3772     | 0.1394      | 0.036*      |
| C15  | 1.0705 (3)  | -0.1817 (3) | 0.1142 (3)  | 0.0265 (7)  |
| C16  | 1.0722 (3)  | -0.0549 (3) | 0.1534 (3)  | 0.0296 (7)  |
| H16A | 1.1246      | 0.0212      | 0.1232      | 0.035*      |
| C17  | 0.9956 (3)  | -0.0444 (3) | 0.2368 (3)  | 0.0303 (7)  |
| H17A | 0.9988      | 0.0396      | 0.2624      | 0.036*      |
| C18  | 1.1368 (4)  | -0.3274 (4) | -0.0096 (3) | 0.0400 (8)  |
| H18A | 1.1633      | -0.3597     | 0.0609      | 0.060*      |
| H18B | 1.1998      | -0.3172     | -0.0617     | 0.060*      |
| H18C | 1.0412      | -0.3928     | -0.0566     | 0.060*      |
| C19  | 1.2199 (4)  | -0.0842 (4) | -0.0251 (3) | 0.0456 (9)  |
| H19A | 1.2955      | -0.0062     | 0.0374      | 0.068*      |
| H19B | 1.1546      | -0.0580     | -0.0667     | 0.068*      |
| H19C | 1.2584      | -0.1150     | -0.0849     | 0.068*      |
| C20  | 0.8178 (4)  | 0.2048 (3)  | 0.5119 (3)  | 0.0373 (8)  |
| H20A | 0.8989      | 0.2051      | 0.4907      | 0.056*      |
| H20B | 0.8488      | 0.2828      | 0.5794      | 0.056*      |

|      |            |            |            |            |
|------|------------|------------|------------|------------|
| H20C | 0.7590     | 0.2104     | 0.4405     | 0.056*     |
| C21  | 0.2694 (3) | 0.4028 (3) | 0.2798 (3) | 0.0255 (6) |
| C22  | 0.2061 (3) | 0.3196 (3) | 0.1602 (3) | 0.0333 (7) |
| H22A | 0.1077     | 0.2714     | 0.1305     | 0.040*     |
| C23  | 0.2884 (3) | 0.3080 (3) | 0.0850 (3) | 0.0313 (7) |
| H23A | 0.2447     | 0.2519     | 0.0046     | 0.038*     |
| C24  | 0.4360 (3) | 0.3785 (3) | 0.1271 (3) | 0.0291 (7) |
| C25  | 0.4974 (3) | 0.4628 (3) | 0.2463 (3) | 0.0300 (7) |
| H25A | 0.5958     | 0.5115     | 0.2759     | 0.036*     |
| C26  | 0.4160 (3) | 0.4765 (3) | 0.3227 (3) | 0.0286 (7) |
| H26A | 0.4595     | 0.5349     | 0.4021     | 0.034*     |
| C27  | 0.5253 (4) | 0.3608 (4) | 0.0459 (3) | 0.0370 (8) |
| H27A | 0.4763     | 0.3403     | -0.0404    | 0.055*     |
| H27B | 0.5420     | 0.2863     | 0.0616     | 0.055*     |
| H27C | 0.6143     | 0.4446     | 0.0649     | 0.055*     |

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|-------------|--------------|--------------|
| S1  | 0.0328 (4)  | 0.0371 (5)  | 0.0331 (4)  | 0.0226 (4)  | 0.0159 (3)   | 0.0132 (4)   |
| O1  | 0.0380 (13) | 0.0384 (13) | 0.0485 (14) | 0.0270 (12) | 0.0196 (11)  | 0.0202 (11)  |
| O2  | 0.0542 (18) | 0.157 (3)   | 0.0318 (15) | 0.068 (2)   | 0.0054 (13)  | -0.0097 (17) |
| O3  | 0.095 (2)   | 0.0431 (16) | 0.127 (3)   | 0.0462 (17) | 0.094 (2)    | 0.0523 (17)  |
| O1W | 0.0345 (12) | 0.0385 (14) | 0.0405 (13) | 0.0194 (11) | 0.0115 (11)  | 0.0084 (11)  |
| N1  | 0.0282 (14) | 0.0278 (14) | 0.0312 (14) | 0.0141 (12) | 0.0091 (11)  | 0.0086 (11)  |
| N2  | 0.0324 (15) | 0.0387 (16) | 0.0352 (15) | 0.0182 (14) | 0.0150 (12)  | 0.0091 (13)  |
| C1  | 0.0221 (15) | 0.0381 (18) | 0.0213 (15) | 0.0142 (14) | 0.0073 (12)  | 0.0086 (13)  |
| C2  | 0.0332 (18) | 0.0310 (18) | 0.0383 (18) | 0.0153 (15) | 0.0120 (15)  | 0.0163 (15)  |
| C3  | 0.0381 (18) | 0.0316 (18) | 0.0392 (19) | 0.0222 (16) | 0.0089 (15)  | 0.0096 (15)  |
| C4  | 0.0285 (17) | 0.044 (2)   | 0.0311 (17) | 0.0186 (16) | 0.0121 (14)  | 0.0109 (15)  |
| C5  | 0.0296 (17) | 0.0341 (18) | 0.0315 (17) | 0.0096 (15) | 0.0088 (14)  | 0.0161 (14)  |
| C6  | 0.0322 (17) | 0.0255 (16) | 0.0257 (16) | 0.0167 (14) | -0.0004 (13) | 0.0022 (12)  |
| C7  | 0.0331 (17) | 0.0292 (18) | 0.0358 (18) | 0.0116 (15) | 0.0110 (15)  | 0.0145 (14)  |
| C8  | 0.0316 (17) | 0.0367 (19) | 0.0280 (16) | 0.0170 (16) | 0.0075 (14)  | 0.0070 (14)  |
| C9  | 0.0240 (15) | 0.0229 (16) | 0.0263 (16) | 0.0122 (13) | 0.0002 (12)  | 0.0035 (12)  |
| C10 | 0.0259 (16) | 0.0324 (18) | 0.0286 (16) | 0.0153 (15) | 0.0085 (13)  | 0.0093 (13)  |
| C11 | 0.0311 (17) | 0.0281 (17) | 0.0328 (17) | 0.0130 (15) | 0.0092 (14)  | 0.0084 (14)  |
| C12 | 0.0270 (16) | 0.0349 (18) | 0.0266 (16) | 0.0157 (15) | 0.0045 (13)  | 0.0062 (14)  |
| C13 | 0.0283 (17) | 0.0358 (19) | 0.0319 (17) | 0.0125 (15) | 0.0066 (14)  | 0.0080 (14)  |
| C14 | 0.0284 (16) | 0.0308 (18) | 0.0344 (17) | 0.0161 (15) | 0.0106 (14)  | 0.0065 (14)  |
| C15 | 0.0231 (15) | 0.0303 (17) | 0.0247 (15) | 0.0135 (14) | 0.0040 (12)  | 0.0038 (13)  |
| C16 | 0.0258 (16) | 0.0288 (17) | 0.0328 (17) | 0.0123 (14) | 0.0058 (13)  | 0.0098 (14)  |
| C17 | 0.0325 (17) | 0.0285 (17) | 0.0297 (17) | 0.0188 (15) | 0.0007 (13)  | 0.0008 (13)  |
| C18 | 0.040 (2)   | 0.049 (2)   | 0.039 (2)   | 0.0293 (19) | 0.0136 (16)  | 0.0030 (16)  |
| C19 | 0.041 (2)   | 0.060 (3)   | 0.045 (2)   | 0.024 (2)   | 0.0236 (17)  | 0.0249 (19)  |
| C20 | 0.0404 (19) | 0.0348 (19) | 0.044 (2)   | 0.0187 (17) | 0.0220 (16)  | 0.0160 (16)  |
| C21 | 0.0289 (16) | 0.0276 (17) | 0.0267 (15) | 0.0172 (14) | 0.0103 (13)  | 0.0113 (13)  |
| C22 | 0.0266 (16) | 0.043 (2)   | 0.0309 (17) | 0.0165 (16) | 0.0082 (14)  | 0.0102 (15)  |

## supplementary materials

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|     |             |             |             |             |             |             |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|
| C23 | 0.0352 (18) | 0.0352 (18) | 0.0227 (16) | 0.0169 (16) | 0.0069 (14) | 0.0065 (13) |
| C24 | 0.0361 (17) | 0.0287 (17) | 0.0334 (17) | 0.0207 (15) | 0.0148 (14) | 0.0157 (14) |
| C25 | 0.0222 (15) | 0.0281 (17) | 0.0388 (18) | 0.0102 (14) | 0.0078 (13) | 0.0132 (14) |
| C26 | 0.0297 (16) | 0.0240 (16) | 0.0303 (16) | 0.0115 (14) | 0.0086 (13) | 0.0063 (13) |
| C27 | 0.0410 (19) | 0.045 (2)   | 0.042 (2)   | 0.0286 (18) | 0.0240 (16) | 0.0208 (16) |

### *Geometric parameters (Å, °)*

|             |             |              |           |
|-------------|-------------|--------------|-----------|
| S1—O3       | 1.433 (3)   | C12—C17      | 1.396 (4) |
| S1—O2       | 1.435 (3)   | C13—C14      | 1.359 (4) |
| S1—O1       | 1.443 (2)   | C13—H13A     | 0.9300    |
| S1—C21      | 1.782 (3)   | C14—C15      | 1.408 (4) |
| O1W—H1W     | 0.8997      | C14—H14A     | 0.9300    |
| O1W—H2W     | 0.8784      | C15—C16      | 1.421 (4) |
| N1—C9       | 1.353 (4)   | C16—C17      | 1.392 (4) |
| N1—C1       | 1.411 (4)   | C16—H16A     | 0.9300    |
| N1—C20      | 1.470 (4)   | C17—H17A     | 0.9300    |
| N2—C15      | 1.368 (4)   | C18—H18A     | 0.9600    |
| N2—C18      | 1.446 (4)   | C18—H18B     | 0.9600    |
| N2—C19      | 1.453 (4)   | C18—H18C     | 0.9600    |
| C1—C2       | 1.395 (4)   | C19—H19A     | 0.9600    |
| C1—C6       | 1.409 (4)   | C19—H19B     | 0.9600    |
| C2—C3       | 1.358 (4)   | C19—H19C     | 0.9600    |
| C2—H2A      | 0.9300      | C20—H20A     | 0.9600    |
| C3—C4       | 1.374 (4)   | C20—H20B     | 0.9600    |
| C3—H3A      | 0.9300      | C20—H20C     | 0.9600    |
| C4—C5       | 1.375 (5)   | C21—C22      | 1.382 (4) |
| C4—H4A      | 0.9300      | C21—C26      | 1.385 (4) |
| C5—C6       | 1.423 (4)   | C22—C23      | 1.376 (4) |
| C5—H5A      | 0.9300      | C22—H22A     | 0.9300    |
| C6—C7       | 1.416 (4)   | C23—C24      | 1.393 (4) |
| C7—C8       | 1.336 (4)   | C23—H23A     | 0.9300    |
| C7—H7A      | 0.9300      | C24—C25      | 1.382 (4) |
| C8—C9       | 1.451 (4)   | C24—C27      | 1.509 (4) |
| C8—H8A      | 0.9300      | C25—C26      | 1.385 (4) |
| C9—C10      | 1.423 (4)   | C25—H25A     | 0.9300    |
| C10—C11     | 1.328 (4)   | C26—H26A     | 0.9300    |
| C10—H10A    | 0.9300      | C27—H27A     | 0.9600    |
| C11—C12     | 1.455 (4)   | C27—H27B     | 0.9600    |
| C11—H11A    | 0.9300      | C27—H27C     | 0.9600    |
| C12—C13     | 1.392 (4)   |              |           |
| O3—S1—O2    | 113.8 (2)   | C13—C14—H14A | 119.1     |
| O3—S1—O1    | 113.16 (16) | C15—C14—H14A | 119.1     |
| O2—S1—O1    | 112.01 (18) | N2—C15—C14   | 121.4 (3) |
| O3—S1—C21   | 105.11 (14) | N2—C15—C16   | 121.8 (3) |
| O2—S1—C21   | 105.52 (15) | C14—C15—C16  | 116.8 (3) |
| O1—S1—C21   | 106.33 (13) | C17—C16—C15  | 120.1 (3) |
| H1W—O1W—H2W | 102.3       | C17—C16—H16A | 119.9     |
| C9—N1—C1    | 123.0 (3)   | C15—C16—H16A | 119.9     |

|              |            |                 |            |
|--------------|------------|-----------------|------------|
| C9—N1—C20    | 119.4 (3)  | C16—C17—C12     | 121.9 (3)  |
| C1—N1—C20    | 117.6 (2)  | C16—C17—H17A    | 119.0      |
| C15—N2—C18   | 120.6 (3)  | C12—C17—H17A    | 119.0      |
| C15—N2—C19   | 120.8 (3)  | N2—C18—H18A     | 109.5      |
| C18—N2—C19   | 117.9 (3)  | N2—C18—H18B     | 109.5      |
| C2—C1—C6     | 119.8 (3)  | H18A—C18—H18B   | 109.5      |
| C2—C1—N1     | 121.8 (3)  | N2—C18—H18C     | 109.5      |
| C6—C1—N1     | 118.4 (3)  | H18A—C18—H18C   | 109.5      |
| C3—C2—C1     | 119.4 (3)  | H18B—C18—H18C   | 109.5      |
| C3—C2—H2A    | 120.3      | N2—C19—H19A     | 109.5      |
| C1—C2—H2A    | 120.3      | N2—C19—H19B     | 109.5      |
| C2—C3—C4     | 122.7 (3)  | H19A—C19—H19B   | 109.5      |
| C2—C3—H3A    | 118.7      | N2—C19—H19C     | 109.5      |
| C4—C3—H3A    | 118.7      | H19A—C19—H19C   | 109.5      |
| C3—C4—C5     | 119.6 (3)  | H19B—C19—H19C   | 109.5      |
| C3—C4—H4A    | 120.2      | N1—C20—H20A     | 109.5      |
| C5—C4—H4A    | 120.2      | N1—C20—H20B     | 109.5      |
| C4—C5—C6     | 119.7 (3)  | H20A—C20—H20B   | 109.5      |
| C4—C5—H5A    | 120.1      | N1—C20—H20C     | 109.5      |
| C6—C5—H5A    | 120.1      | H20A—C20—H20C   | 109.5      |
| C1—C6—C7     | 119.2 (3)  | H20B—C20—H20C   | 109.5      |
| C1—C6—C5     | 118.8 (3)  | C22—C21—C26     | 119.7 (3)  |
| C7—C6—C5     | 122.0 (3)  | C22—C21—S1      | 119.5 (2)  |
| C8—C7—C6     | 120.4 (3)  | C26—C21—S1      | 120.8 (2)  |
| C8—C7—H7A    | 119.8      | C23—C22—C21     | 120.1 (3)  |
| C6—C7—H7A    | 119.8      | C23—C22—H22A    | 120.0      |
| C7—C8—C9     | 121.9 (3)  | C21—C22—H22A    | 120.0      |
| C7—C8—H8A    | 119.0      | C22—C23—C24     | 121.2 (3)  |
| C9—C8—H8A    | 119.0      | C22—C23—H23A    | 119.4      |
| N1—C9—C10    | 122.7 (3)  | C24—C23—H23A    | 119.4      |
| N1—C9—C8     | 116.9 (3)  | C25—C24—C23     | 117.8 (3)  |
| C10—C9—C8    | 120.4 (3)  | C25—C24—C27     | 121.3 (3)  |
| C11—C10—C9   | 126.0 (3)  | C23—C24—C27     | 120.9 (3)  |
| C11—C10—H10A | 117.0      | C24—C25—C26     | 121.6 (3)  |
| C9—C10—H10A  | 117.0      | C24—C25—H25A    | 119.2      |
| C10—C11—C12  | 127.1 (3)  | C26—C25—H25A    | 119.2      |
| C10—C11—H11A | 116.4      | C21—C26—C25     | 119.5 (3)  |
| C12—C11—H11A | 116.4      | C21—C26—H26A    | 120.3      |
| C13—C12—C17  | 117.2 (3)  | C25—C26—H26A    | 120.3      |
| C13—C12—C11  | 119.0 (3)  | C24—C27—H27A    | 109.5      |
| C17—C12—C11  | 123.8 (3)  | C24—C27—H27B    | 109.5      |
| C14—C13—C12  | 122.2 (3)  | H27A—C27—H27B   | 109.5      |
| C14—C13—H13A | 118.9      | C24—C27—H27C    | 109.5      |
| C12—C13—H13A | 118.9      | H27A—C27—H27C   | 109.5      |
| C13—C14—C15  | 121.9 (3)  | H27B—C27—H27C   | 109.5      |
| C9—N1—C1—C2  | -178.0 (3) | C11—C12—C13—C14 | -178.1 (3) |
| C20—N1—C1—C2 | 1.2 (4)    | C12—C13—C14—C15 | -0.2 (5)   |
| C9—N1—C1—C6  | 0.9 (4)    | C18—N2—C15—C14  | 3.6 (4)    |
| C20—N1—C1—C6 | -179.9 (3) | C19—N2—C15—C14  | 174.2 (3)  |

## supplementary materials

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| C6—C1—C2—C3     | 0.3 (4)    | C18—N2—C15—C16  | -176.9 (3) |
| N1—C1—C2—C3     | 179.2 (3)  | C19—N2—C15—C16  | -6.3 (4)   |
| C1—C2—C3—C4     | -0.6 (5)   | C13—C14—C15—N2  | 179.6 (3)  |
| C2—C3—C4—C5     | 0.5 (5)    | C13—C14—C15—C16 | 0.1 (4)    |
| C3—C4—C5—C6     | -0.2 (5)   | N2—C15—C16—C17  | -179.1 (3) |
| C2—C1—C6—C7     | -179.6 (3) | C14—C15—C16—C17 | 0.4 (4)    |
| N1—C1—C6—C7     | 1.5 (4)    | C15—C16—C17—C12 | -0.9 (4)   |
| C2—C1—C6—C5     | 0.0 (4)    | C13—C12—C17—C16 | 0.7 (4)    |
| N1—C1—C6—C5     | -178.9 (3) | C11—C12—C17—C16 | 178.6 (3)  |
| C4—C5—C6—C1     | -0.1 (4)   | O3—S1—C21—C22   | 53.9 (3)   |
| C4—C5—C6—C7     | 179.5 (3)  | O2—S1—C21—C22   | 174.5 (3)  |
| C1—C6—C7—C8     | -1.3 (4)   | O1—S1—C21—C22   | -66.3 (3)  |
| C5—C6—C7—C8     | 179.2 (3)  | O3—S1—C21—C26   | -125.2 (3) |
| C6—C7—C8—C9     | -1.3 (5)   | O2—S1—C21—C26   | -4.6 (3)   |
| C1—N1—C9—C10    | 176.0 (3)  | O1—S1—C21—C26   | 114.6 (2)  |
| C20—N1—C9—C10   | -3.3 (4)   | C26—C21—C22—C23 | 1.4 (5)    |
| C1—N1—C9—C8     | -3.3 (4)   | S1—C21—C22—C23  | -177.7 (2) |
| C20—N1—C9—C8    | 177.5 (3)  | C21—C22—C23—C24 | 0.2 (5)    |
| C7—C8—C9—N1     | 3.5 (4)    | C22—C23—C24—C25 | -1.1 (5)   |
| C7—C8—C9—C10    | -175.8 (3) | C22—C23—C24—C27 | 177.6 (3)  |
| N1—C9—C10—C11   | -179.3 (3) | C23—C24—C25—C26 | 0.6 (4)    |
| C8—C9—C10—C11   | -0.1 (5)   | C27—C24—C25—C26 | -178.1 (3) |
| C9—C10—C11—C12  | 179.5 (3)  | C22—C21—C26—C25 | -1.9 (4)   |
| C10—C11—C12—C13 | -179.7 (3) | S1—C21—C26—C25  | 177.2 (2)  |
| C10—C11—C12—C17 | 2.4 (5)    | C24—C25—C26—C21 | 0.9 (4)    |
| C17—C12—C13—C14 | -0.2 (5)   |                 |            |

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

| <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> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1W—H1W $\cdots$ O2                 | 0.90        | 1.96                | 2.839 (4)                  | 164                           |
| O1W—H2W $\cdots$ O1 <sup>i</sup>    | 0.88        | 2.01                | 2.893 (3)                  | 179                           |
| C10—H10A $\cdots$ O3 <sup>ii</sup>  | 0.93        | 2.57                | 3.460 (4)                  | 162                           |
| C17—H17A $\cdots$ O3 <sup>ii</sup>  | 0.93        | 2.45                | 3.344 (5)                  | 163                           |
| C20—H20A $\cdots$ O3 <sup>ii</sup>  | 0.96        | 2.33                | 3.204 (6)                  | 151                           |
| C20—H20B $\cdots$ O1 <sup>iii</sup> | 0.96        | 2.49                | 3.388 (4)                  | 156                           |
| C26—H26A $\cdots$ O2                | 0.93        | 2.51                | 2.884 (5)                  | 104                           |
| C7—H7A $\cdots$ Cg4 <sup>iv</sup>   | 0.93        | 2.97                | 3.615 (4)                  | 128                           |
| C23—H23A $\cdots$ Cg3 <sup>v</sup>  | 0.93        | 2.82                | 3.594 (4)                  | 141                           |

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

Fig. 1

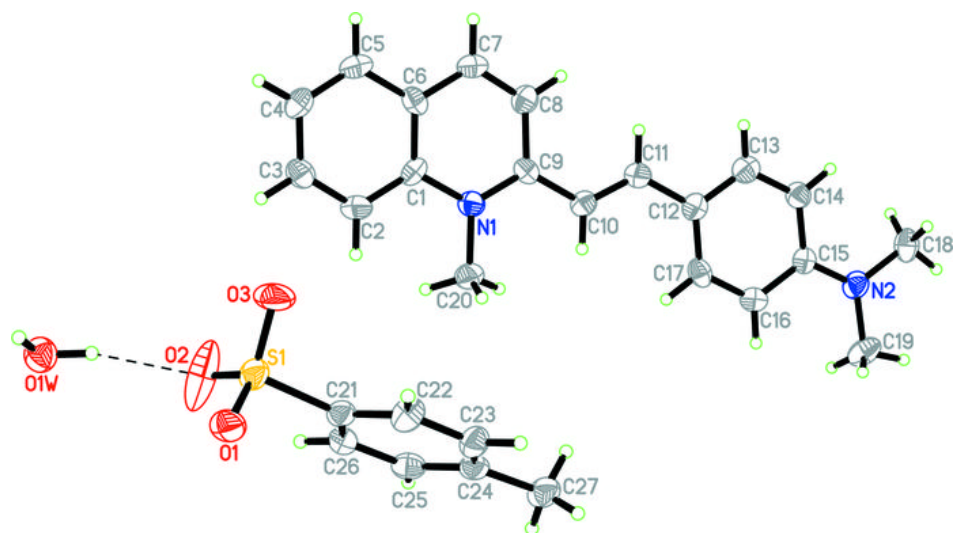


Fig. 2

