# organic compounds

# (E)-2-[4-(Dimethylamino)styryl]-1-methylquinolinium 4-methylbenzene-sulfonate monohydrate[1]

## Thawanrat Kobkeatthawin,[a] Thitipone Suwunwong,[a] Suchada Chantrapromma[a]* and Hoong-Kun Fun[b]§

[a]Crystal Materials Research Unit, Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: suchada.c@psu.ac.th

In the title compound, $C_{20}H_{21}N_2{}^+ \cdot C_7H_7O_3S^- \cdot H_2O$, the cation is essentially planar, as indicated by the dihedral angle of 2.79 (13)° between the quinolinium and the dimethylaminophenyl 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 C—H···O hydrogen bonds and the anion is further linked with the water molecule by O—H···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 C—H···$\pi$ interactions involving the dimethylaminophenyl and methyl-phenyl 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).
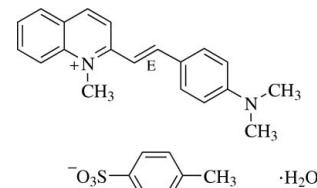


## Experimental

### Crystal data

| | |
|---|---|
| $C_{20}H_{21}N_2{}^+ \cdot C_7H_7O_3S^- \cdot H_2O$ | $\gamma$ = 117.021 (3)° |
| $M_r$ = 478.60 | $V$ = 1169.78 (13) Å$^3$ |
| Triclinic, $P\bar{1}$ | $Z$ = 2 |
| $a$ = 10.9739 (5) Å | Mo $K\alpha$ radiation |
| $b$ = 11.1789 (5) Å | $\mu$ = 0.18 mm$^{-1}$ |
| $c$ = 11.1923 (9) Å | $T$ = 100.0 (1) K |
| $\alpha$ = 97.133 (5)° | 0.24 × 0.19 × 0.08 mm |
| $\beta$ = 100.322 (5)° | |

### Data collection

| | |
|---|---|
| Bruker SMART APEX2 CCD area-detector diffractometer | 17557 measured reflections |
| | 5390 independent reflections |
| Absorption correction: multi-scan (SADABS; Bruker, 2005) | 3272 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.958, $T_{max}$ = 0.986 | $R_{int}$ = 0.073 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.072 | 311 parameters |
| $wR(F^2)$ = 0.203 | H-atom parameters constrained |
| $S$ = 1.05 | $\Delta\rho_{max}$ = 0.60 e Å$^{-3}$ |
| 5390 reflections | $\Delta\rho_{min}$ = −0.47 e Å$^{-3}$ |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1W—H1W···O2 | 0.90 | 1.96 | 2.839 (4) | 164 |
| O1W—H2W···O1$^i$ | 0.88 | 2.01 | 2.893 (3) | 179 |
| C10—H10A···O3$^{ii}$ | 0.93 | 2.57 | 3.460 (4) | 162 |
| C17—H17A···O3$^{ii}$ | 0.93 | 2.45 | 3.344 (5) | 163 |
| C20—H20A···O3$^{ii}$ | 0.96 | 2.33 | 3.204 (6) | 151 |
| C20—H20B···O1$^{iii}$ | 0.96 | 2.49 | 3.388 (5) | 156 |
| C26—H26A···O2 | 0.93 | 2.51 | 2.884 (5) | 104 |
| C7—H7A···Cg4$^{iv}$ | 0.93 | 2.97 | 3.615 (4) | 128 |
| C23—H23A···Cg3$^v$ | 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).

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

## References

Adachi, H., Takanishi, Y., Yabuzaki, J., Mori, Y. & Sasaki, T. (1999). *J. Cryst. Growth*, **158/159**, 568–571.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Chantrapromma, S., Kobkeatthawin, T., Chanawanno, K., Karalai, C. & Fun, H.-K. (2008). *Acta Cryst.* E**64**, o876–o877.

Dittrich, Ph., Bartlome, R., Montemezzani, G. & Günter, P. (2003). *Appl. Surf. Sci.* **220**, 88–95.

Nogi, K., Anwar, U., Tsuji, K., Duan, X.-M., Okada, S., Oikawa, H., Matsuda, H. & Nakanishi, H. (2000). *Nonlinear Optics*. **24**, 35–40.

Ogawa, J., Okada, S., Glavcheva, Z. & Nakanishi, H. (2008). *J. Cryst. Growth*, **310**, 836–842.

Otero, M., Herranz, M. A., Seoane, C., Martín, N., Garín, J., Orduna, J., Alcalá, R. & Villacampa, B. (2002). *Tetrahedron*, **58**, 7463–7475.

Rahman, A. A., Razak, I. A., Fun, H.-K., Saenee, P., Jindawong, B., Chantrapromma, S. & Karalai, C. (2003). *Acta Cryst.* E**59**, o1798–o1800.

Sato, N., Rikukawa, M., Sanui, K. & Ogata, N. (1999). *Synth. Met.* **101**, 132–133.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Weir, C. A. M., Hadizad, T., Beaudin, A. M. R. & Wang, Z.-Y. (2003). *Tetrahedron Lett.* **44**, 4697–4700.

Yang, Z., Wörle, M., Mutter, L., Jazbinsek, M. & Günter, P. (2007). *Cryst. Growth Des.* **7**, 83–86.

# supporting information

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

**Thawanrat Kobkeatthawin, Thitipone Suwunwong, Suchada Chantrapromma and Hoong-Kun Fun**

### S1. 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 hyperpolariability ($\beta$) 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 hyperpolariability 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⋯O hydrogen bonded to water molecule, the atom O2 of the sulfonate also contributed to a weak intramolecular C26—H26A⋯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⋯O interactions (Table 1). The cation is linked to the anion by weak C—H⋯O interactions and the anion is further linked to the water molecule by O—H⋯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⋯$\pi$ 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.

## S2. 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*-toluensulfonate (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 recrystalized from methanol by slow evaporation of the solvent at room temperature a few weeks (m.p. 557–558 K).

## S3. Refinement

All H atoms were placed in calculated positions, with d(O—H) = 0.88–0.90 Å, $U_{iso}$(H) = $1.5U_{eq}$(O), d(C—H) = 0.93 Å, $U_{iso}$(H) = $1.2U_{eq}$(C) for aromatic and CH, and 0.96 Å, $U_{iso}$(H) = $1.5U_{eq}$(C) for $CH_3$ atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.98 Å from C8 and the deepest hole is located at 0.96 Å from S1.
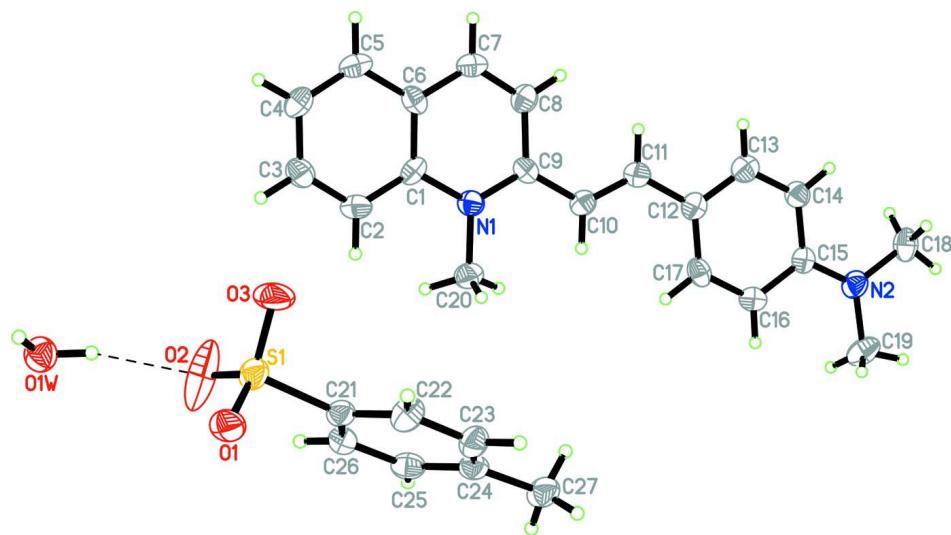


**Figure 1**

The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.
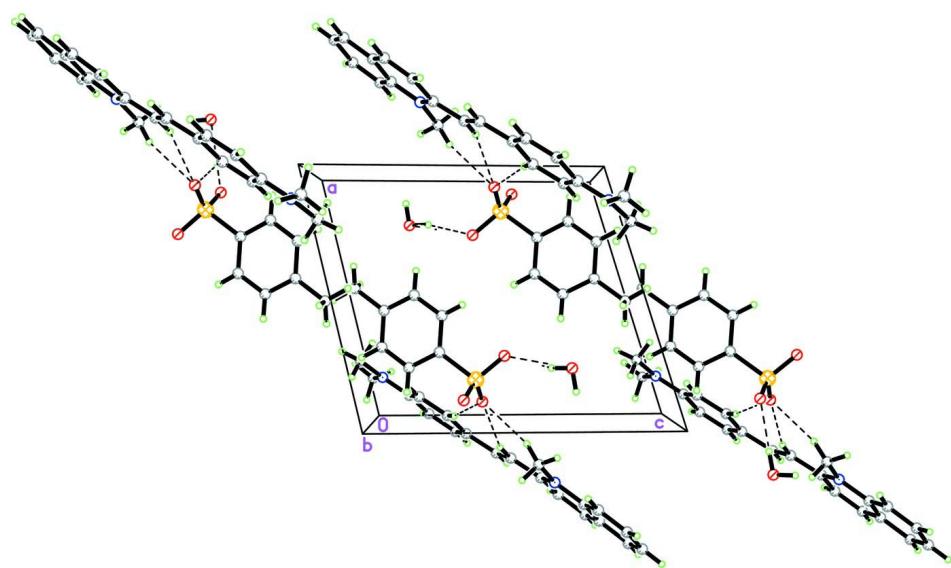
**Figure 2**

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*

| | |
|---|---|
| $C_{20}H_{21}N_2^+ \cdot C_7H_7O_3S^- \cdot H_2O$ | $Z = 2$ |
| $M_r = 478.60$ | $F(000) = 508$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.359$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Melting point = 557–558 K |
| $a = 10.9739$ (5) Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| $b = 11.1789$ (5) Å | Cell parameters from 5390 reflections |
| $c = 11.1923$ (9) Å | $\theta = 1.2$–27.5° |
| $\alpha = 97.133$ (5)° | $\mu = 0.18$ mm$^{-1}$ |
| $\beta = 100.322$ (5)° | $T = 100$ K |
| $\gamma = 117.021$ (3)° | Block, green |
| $V = 1169.78$ (13) Å$^3$ | $0.24 \times 0.19 \times 0.08$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART APEX2 CCD area-detector diffractometer | 17557 measured reflections |
| | 5390 independent reflections |
| Radiation source: fine-focus sealed tube | 3272 reflections with $I > 2\sigma(I)$ |
| Graphite monochromator | $R_{int} = 0.073$ |
| Detector resolution: 8.33 pixels mm$^{-1}$ | $\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$ |
| $\omega$ scans | $h = -14 \rightarrow 14$ |
| Absorption correction: multi-scan | $k = -14 \rightarrow 14$ |
| (*SADABS*; Bruker, 2005) | $l = -14 \rightarrow 11$ |
| $T_{min} = 0.958$, $T_{max} = 0.986$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $S = 1.05$ |
| Least-squares matrix: full | 5390 reflections |
| $R[F^2 > 2\sigma(F^2)] = 0.072$ | 311 parameters |
| $wR(F^2) = 0.203$ | 0 restraints |

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.60$ e Å$^{-3}$
$\Delta\rho_{min} = -0.47$ e Å$^{-3}$

*Special details*

**Experimental**. The low-temparture 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 (Å²)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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) |
| 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, º)*

| | | | |
|------|----------|----------|----------|
| 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) |
| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1*W*—H1*W*···O2 | 0.90 | 1.96 | 2.839 (4) | 164 |
| O1*W*—H2*W*···O1[i] | 0.88 | 2.01 | 2.893 (3) | 179 |
| C10—H10*A*···O3[ii] | 0.93 | 2.57 | 3.460 (4) | 162 |
| C17—H17*A*···O3[ii] | 0.93 | 2.45 | 3.344 (5) | 163 |
| C20—H20*A*···O3[ii] | 0.96 | 2.33 | 3.204 (6) | 151 |
| C20—H20*B*···O1[iii] | 0.96 | 2.49 | 3.388 (4) | 156 |
| C26—H26*A*···O2 | 0.93 | 2.51 | 2.884 (5) | 104 |
| C7—H7*A*···*Cg*4[iv] | 0.93 | 2.97 | 3.615 (4) | 128 |
| C23—H23*A*···*Cg*3[v] | 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*.