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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.045
 wR factor = 0.126
 Data-to-parameter ratio = 16.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

trans-4-[(4-Dimethylaminophenyl)ethenyl]-*N*-methylquinolinium *p*-toluenesulfonate monohydrate

In the title salt, $\text{C}_{20}\text{H}_{21}\text{N}_2^+ \cdot \text{C}_7\text{H}_7\text{SO}_3^- \cdot \text{H}_2\text{O}$, the quinolinium cation exhibits a large molecular non-linear optical (NLO) response, as determined by Stark spectroscopy, but crystallization in the centrosymmetric space group $P\bar{1}$ precludes significant bulk NLO effects. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding links the constituent molecules into a three-dimensional network.

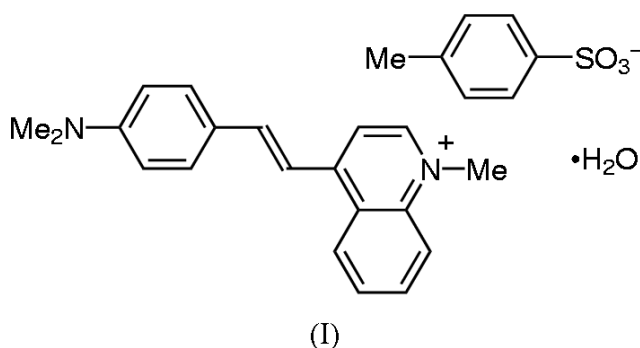
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Comment

The synthesis and study of molecular compounds with non-linear optical (NLO) properties has attracted much attention, because such materials hold promise for applications in optoelectronic and photonic devices (Bosshard *et al.*, 1995; Nalwa & Miyata, 1997). In order to create efficient quadratic (second-order) NLO materials, both the molecular and bulk properties must be optimized. The majority of promising compounds constitute dipolar donor- π -acceptor (*D*- π -*A*) molecules and these must be arranged noncentrosymmetrically in order to afford macroscopic structures capable of showing bulk quadratic NLO effects, such as frequency doubling (second-harmonic generation, SHG).



Within the diverse range of existing NLO compounds, stilbazolium salts are particularly attractive for device applications (Lee & Kim, 1999). The archetypal compound *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium *para*-toluenesulfonate (DAST) displays very marked bulk quadratic NLO activity, as originally shown by powder SHG studies (Marder *et al.*, 1989, 1994). At the molecular level, quadratic NLO effects are determined by first hyperpolarizabilities β , and static ('off-resonance') first hyperpolarizabilities β_0 are normally used when comparing active compounds. Hyper-Rayleigh scattering experiments with DAST using a 1064 nm laser yielded a large β_0 value of 364×10^{-30} esu (Duan *et al.*,

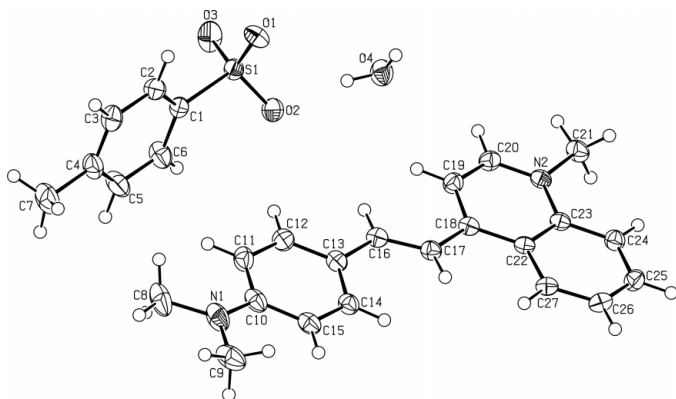


Figure 1
A representation of the molecular structure of (I), with 50% probability displacement ellipsoids.

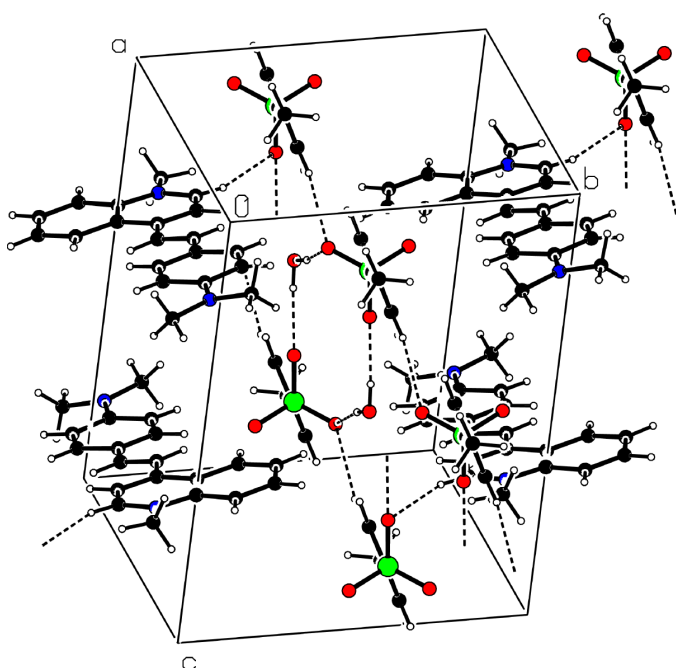


Figure 2
A representation of the hydrogen-bonding interactions (dashed lines) in (I).

1995). DAST has therefore been intensively investigated over recent years (Meier *et al.*, 2000; Kaino *et al.*, 2002), including the growth of large high-quality single crystals (Pan *et al.*, 1996; Sohma *et al.*, 1999; Mohan Kumar *et al.*, 2003), and the demonstration of prototype NLO devices for parametric interactions and electro-optical modulation (Meier *et al.* 1998; Bhowmik *et al.* 2000; Geis *et al.* 2004; Taniuchi *et al.* 2004).

In addition to their NLO properties, *D*- π -*A* molecules display intense low-energy absorption bands which arise from $\pi(D) \rightarrow \pi^*(A)$ intramolecular charge-transfer (ICT) excitations. A two-state model (Oudar & Chemla, 1977; Zyss & Oudar, 1982) shows that β_0 is proportional to the product of the square of the ICT transition dipole moment μ_{12} and the dipole moment change $\Delta\mu_{12}$, and inversely proportional to

the square of the ICT energy E_{\max} . Therefore, β_0 increases with increasing intensity and decreasing energy of the ICT absorption. The ICT band of the PF_6^- salt of the cation in (I) ($[\text{DAQ}^+]\text{PF}_6^-$) is red-shifted by *ca* 0.34 eV, but is *ca* 85% as intense, when compared with that of the PF_6^- salt of the chromophore in DAST ($[\text{DAS}^+]\text{PF}_6^-$; $\lambda_{\max} = 470$ nm, $\epsilon = 42\,800\text{ M}^{-1}\text{ dm}^3$ in acetonitrile; Coe *et al.*, 2002). This marked red-shifting suggests that the β_0 value of (I) may be larger than that of DAST. We have previously determined β_0 for $[\text{DAS}^+]\text{PF}_6^-$ using Stark (electroabsorption) spectroscopy (Coe *et al.*, 2003), and have now applied the same approach to $[\text{DAQ}^+]\text{PF}_6^-$. By applying the two-state equation $\beta_0 = 3\Delta\mu_{12}(\mu_{12})^2/(E_{\max})^2$ to data obtained from butyronitrile glasses at 77 K, the results are 236 and 255×10^{-30} esu for $[\text{DAS}^+]\text{PF}_6^-$ and $[\text{DAQ}^+]\text{PF}_6^-$, respectively. The lower-than-expected increase in β_0 is attributable to a decrease in $\Delta\mu_{12}$ from 16.3 to 13.3 D on moving from $[\text{DAS}^+]\text{PF}_6^-$ to $[\text{DAQ}^+]\text{PF}_6^-$, whilst μ_{12} remains constant at 9.1 D.

The molecular structure of the cation in (I) is as indicated by ^1H NMR spectroscopy, and similar to that observed previously in the corresponding hexamolybdate salt (Xu *et al.*, 1995), although the precision of the present structure is rather higher. The conjugated aromatic system is essentially planar, with a maximum deviation from the mean plane of 0.094 Å for atom C24, and this plane forms an angle of 77.48 (6)° with the benzene ring plane of the tosylate anion.

The crystal packing structure of (I) is critical in relation to quadratic NLO properties. DAST crystallizes noncentrosymmetrically in the space group *Cc* (Marder *et al.*, 1989), but unfortunately (I) adopts the centrosymmetric space group *P1* and is hence not suitable for bulk NLO effects. Perhaps not unexpectedly, replacement of the pyridinium ring in DAST with a quinolinium group changes the crystallization behaviour. In fact, the presence of water molecules within the crystal structure of (I) leads to a network of hydrogen bonds involving water, the tosylate anion and the chromophoric cation. The water molecules and tosylate anions form centrosymmetric $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded rings, and weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link these rings to the quinolinium moieties to form a three-dimensional network (Fig. 2).

It has been proposed that the natural tendency towards antiparallel dipole alignment between the cations in DAST is overcome by the presence of the intervening tosylate anions (Marder *et al.*, 1989, 1994), but such an effect is not evident in (I). Although this outcome is rather disappointing, salts of the cation in (I) with other anions may well adopt different crystal structures capable of showing bulk NLO behaviour.

Experimental

The compound *trans*-4-[(4-dimethylaminophenyl)-2-ethenyl]-*N*-methylquinolinium iodide (Bahner *et al.*, 1951) was synthesized by adapting a method which has been applied previously to the analogous dibutylamine compound (Alain *et al.*, 2000). Piperidine (3 drops)

was added to a solution of 4-methyl-*N*-methylquinolinium iodide (276 mg, 0.968 mmol) and 4-(dimethylamino)benzaldehyde (289 mg, 1.937 mmol) in methanol (20 ml). The solution immediately turned purple and was stirred under reflux for 4 h. After cooling to room temperature, the solution was added dropwise to diethyl ether to afford a dark precipitate which was filtered off, washed with diethyl ether and then water, and dried under vacuum (yield 349 mg, 87%). A portion of this crude material (125 mg, 0.300 mmol) was metathesized to (I) by precipitation from water–aqueous sodium *para*-toluenesulfonate (yield 115 mg, 83%). Compound (I) has been reported previously (Metzger *et al.*, 1969). Crystals of (I) suitable for single-crystal X-ray diffraction measurements were obtained by slow diffusion of diethyl ether vapour into a methanol solution of (I) at room temperature; note that the same method is used to produce SHG-active crystals of DAST (Marder *et al.*, 1994). Analysis, found: C 67.99, H 6.35, N 5.86, S 6.69%; calculated for C₂₇H₂₈N₂O₃S·H₂O: C 67.76, H 6.32, N 5.85, S 6.70%. For spectroscopic studies, a portion of the crude iodide salt was also metathesized to the hexafluorophosphate (previously unreported, to our knowledge) by precipitation from water–aqueous ammonium hexafluorophosphate. Analysis, found: C 55.19, H 4.63, N 6.33%, calculated for C₂₀H₂₁F₆N₂P: C 55.30, H 4.87, N 6.45%. Spectroscopic analysis: ¹H NMR (200 MHz, CD₃COCD₃, δ, p.p.m.): 9.12 (1H, *d*, *J* = 6.8 Hz, C₅H₂N), 9.02 (1H, *d*, *J* = 8.5 Hz, C₆H₄), 8.46 (1H, *d*, *J* = 8.4 Hz, C₆H₄), 8.38 (1H, *d*, *J* = 6.6 Hz, C₅H₂N), 8.27 (1H, *t*, *J* = 7.9 Hz, C₆H₄), 8.21 (1H, *d*, *J* = 15.7 Hz, CH), 8.08 (1H, *d*, *J* = 16.2 Hz, CH), 8.03 (1H, *t*, *J* = 7.7 Hz, C₆H₄), 7.86 (2H, *d*, *J* = 9.0 Hz, C₆H₄–NMe₂), 6.86 (2H, *d*, *J* = 9.1 Hz, C₆H₄–NMe₂), 4.68 (3H, *s*, Me), 3.13 (6H, *s*, NMe₂); λ_{max} (nm) [ε (M⁻¹ dm³)] (MeCN): 540 (36 700), 306 (12 400), 242 (17 900).

Crystal data

C₂₀H₂₁N₂⁺·C₇H₇O₃S⁻·H₂O Z = 2
M_r = 478.59 D_x = 1.351 Mg m⁻³
Triclinic, P $\bar{1}$ Mo K α radiation
a = 8.033 (4) Å Cell parameters from 4905 reflections
b = 10.550 (7) Å θ = 2.9–27.5°
c = 14.662 (9) Å μ = 0.18 mm⁻¹
 α = 97.75 (7)° T = 120 (2) K
 β = 97.87 (4)° Slab, dark green
 γ = 103.97 (5)° 0.6 × 0.4 × 0.14 mm
V = 1176.2 (12) Å³

Data collection

Bruker-Nonius KappaCCD area-detector diffractometer 5337 independent reflections
4160 reflections with *I* > 2σ(*I*)
 φ and ω scans R_{int} = 0.041
Absorption correction: multi-scan (SADABS; Sheldrick, 2003) θ_{max} = 27.5°
T_{min} = 0.902, T_{max} = 0.976 *h* = -10 → 10
22 326 measured reflections *k* = -13 → 13
l = -19 → 18

Refinement

Refinement on F² w = 1/[σ²(F_o²) + (0.0684P)² + 0.4268P]
R[F² > 2σ(F²)] = 0.045 where P = (F_o² + 2F_c²)/3
wR(F²) = 0.126 (Δ/σ)_{max} = 0.047
S = 1.02 Δρ_{max} = 0.28 e Å⁻³
5337 reflections Δρ_{min} = -0.53 e Å⁻³
320 parameters Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement Extinction coefficient: 0.016 (4)

Table 1

Selected geometric parameters (Å, °).

C8–N1	1.453 (3)	C18–C19	1.390 (2)
C9–N1	1.444 (3)	C18–C22	1.433 (2)
C10–N1	1.368 (2)	C19–C20	1.372 (2)
C10–C11	1.400 (3)	C20–N2	1.328 (2)
C10–C15	1.413 (3)	C21–N2	1.473 (2)
C11–C12	1.379 (3)	C22–C27	1.414 (2)
C12–C13	1.399 (2)	C22–C23	1.418 (2)
C13–C14	1.404 (3)	C23–N2	1.379 (2)
C13–C16	1.447 (2)	C23–C24	1.405 (2)
C14–C15	1.375 (2)	C24–C25	1.366 (2)
C16–C17	1.348 (2)	C25–C26	1.398 (3)
C17–C18	1.447 (2)	C26–C27	1.365 (2)
N1–C10–C11	120.83 (17)	C27–C22–C23	117.05 (15)
N1–C10–C15	121.65 (17)	C27–C22–C18	122.72 (14)
C11–C10–C15	117.51 (16)	C23–C22–C18	120.21 (14)
C12–C11–C10	120.62 (17)	N2–C23–C24	120.25 (14)
C11–C12–C13	122.12 (17)	N2–C23–C22	118.87 (15)
C12–C13–C14	117.18 (15)	C24–C23–C22	120.87 (15)
C12–C13–C16	119.35 (16)	C25–C24–C23	119.84 (15)
C14–C13–C16	123.45 (16)	C24–C25–C26	120.22 (16)
C15–C14–C13	121.21 (16)	C27–C26–C25	120.68 (15)
C14–C15–C10	121.29 (17)	C26–C27–C22	121.24 (15)
C17–C16–C13	127.15 (15)	C10–N1–C9	121.38 (17)
C16–C17–C18	124.17 (15)	C10–N1–C8	120.21 (18)
C19–C18–C22	116.75 (15)	C9–N1–C8	117.97 (17)
C19–C18–C17	121.72 (15)	C20–N2–C23	120.50 (14)
C22–C18–C17	121.53 (14)	C20–N2–C21	118.80 (14)
C20–C19–C18	120.79 (16)	C23–N2–C21	120.61 (14)
N2–C20–C19	122.84 (15)		

Table 2

Hydrogen-bond geometry (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O4–H2O···O1 ⁱ	0.86 (2)	2.07 (2)	2.922 (3)	175 (2)
O4–H10···O2	0.89 (2)	1.95 (3)	2.838 (3)	169 (2)
C14–H14···O3	0.95	2.41	3.359 (3)	174
C17–H17···O3	0.95	2.49	3.435 (3)	175
C27–H27···O3	0.95	2.34	3.282 (3)	172
C3–H3···O2 ⁱⁱ	0.95	2.59	3.535 (3)	171
C20–H20···O1 ⁱⁱⁱ	0.95	2.37	3.290 (3)	162

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

The H atoms of the water molecule were refined independently with isotropic displacement parameters. H atoms bonded to C atoms were placed in calculated positions, with C–H distances of 0.95 Å [0.98 Å for methyl], and included in the refinement in a riding-model approximation, with U_{iso} = 1.2U_{eq}(C), or 1.5U_{eq}(C) for methyl groups.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97.

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supporting information

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***trans*-4-[(4-Dimethylaminophenyl)ethenyl]-*N*-methylquinolinium *p*-toluene-sulfonate monohydrate**

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trans-4-[(4-Dimethylaminophenyl)ethenyl]-*N*-methylquinolinium *p*-toluenesulfonate monohydrate

Crystal data

$C_{20}H_{21}N_2^+ \cdot C_7H_7O_3S^- \cdot H_2O$

$M_r = 478.59$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 8.033$ (4) Å

$b = 10.550$ (7) Å

$c = 14.662$ (9) Å

$\alpha = 97.75$ (7)°

$\beta = 97.87$ (4)°

$\gamma = 103.97$ (5)°

$V = 1176.2$ (12) Å³

$Z = 2$

$F(000) = 508$

$D_x = 1.351$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4905 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 0.18$ mm⁻¹

$T = 120$ K

Slab, dark green

$0.6 \times 0.4 \times 0.14$ mm

Data collection

Bruker-Nonius KappaCCD area-detector diffractometer

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.902$, $T_{\max} = 0.976$

22326 measured reflections

5337 independent reflections

4160 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.2$ °

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -19 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.126$

$S = 1.02$

5337 reflections

320 parameters

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 atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.4268P]$

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

$(\Delta/\sigma)_{\max} = 0.047$

$\Delta\rho_{\max} = 0.28$ e Å⁻³

$\Delta\rho_{\min} = -0.53$ e Å⁻³

Extinction correction: SHELXL97 (Sheldrick, 1997), $F_c^* = kFc[1 + 0.001xFe^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.016 (4)

Special details

Experimental. The Tmin and Tmax values reported are those calculated from the *SHELX SIZE* command. The ratio of experimental transmission factors from *SADABS* is 0.724295.

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1870 (2)	0.49093 (15)	0.22545 (11)	0.0239 (3)
C2	0.0344 (2)	0.50065 (17)	0.25634 (12)	0.0289 (4)
H2	0.0382	0.538	0.3195	0.035*
C3	-0.1235 (2)	0.45625 (18)	0.19555 (13)	0.0323 (4)
H3	-0.2272	0.4648	0.2171	0.039*
C4	-0.1321 (2)	0.39965 (18)	0.10393 (13)	0.0345 (4)
C5	0.0215 (3)	0.3901 (2)	0.07428 (13)	0.0433 (5)
H5	0.0175	0.3516	0.0113	0.052*
C6	0.1807 (2)	0.4353 (2)	0.13394 (12)	0.0363 (4)
H6	0.2846	0.4281	0.1121	0.044*
C7	-0.3049 (3)	0.3485 (2)	0.03880 (16)	0.0515 (6)
H7A	-0.383	0.2823	0.0653	0.077*
H7B	-0.2874	0.3076	-0.022	0.077*
H7C	-0.3567	0.4222	0.0307	0.077*
C8	-0.2581 (3)	1.0018 (3)	0.06957 (14)	0.0482 (5)
H8A	-0.2393	1.083	0.1152	0.072*
H8B	-0.3833	0.9591	0.0516	0.072*
H8C	-0.2099	1.0239	0.0141	0.072*
C9	-0.2729 (2)	0.7774 (2)	0.10750 (15)	0.0456 (5)
H9A	-0.2615	0.721	0.0511	0.068*
H9B	-0.3956	0.7759	0.1061	0.068*
H9C	-0.2302	0.7441	0.163	0.068*
C10	0.0046 (2)	0.94966 (19)	0.14200 (11)	0.0309 (4)
C11	0.0997 (2)	1.08193 (19)	0.15017 (12)	0.0325 (4)
H11	0.0428	1.1451	0.1301	0.039*
C12	0.2753 (2)	1.12140 (18)	0.18701 (12)	0.0297 (4)
H12	0.3365	1.212	0.1925	0.036*
C13	0.3662 (2)	1.03238 (16)	0.21654 (11)	0.0259 (3)
C14	0.2719 (2)	0.89901 (17)	0.20550 (11)	0.0269 (4)
H14	0.3301	0.8355	0.2235	0.032*
C15	0.0966 (2)	0.85853 (18)	0.16909 (11)	0.0293 (4)
H15	0.0364	0.7675	0.162	0.035*
C16	0.5484 (2)	1.08135 (16)	0.25871 (11)	0.0252 (3)

H16	0.6008	1.1726	0.2599	0.03*
C17	0.6520 (2)	1.01168 (16)	0.29644 (11)	0.0245 (3)
H17	0.6014	0.9209	0.2978	0.029*
C18	0.83523 (19)	1.06637 (15)	0.33494 (11)	0.0226 (3)
C19	0.9158 (2)	1.20092 (16)	0.34417 (12)	0.0267 (3)
H19	0.8495	1.259	0.3249	0.032*
C20	1.0898 (2)	1.25077 (15)	0.38084 (11)	0.0260 (3)
H20	1.1401	1.3434	0.3872	0.031*
C21	1.3748 (2)	1.23849 (17)	0.44935 (12)	0.0298 (4)
H21A	1.3997	1.3342	0.4498	0.045*
H21B	1.4499	1.2011	0.4123	0.045*
H21C	1.3973	1.2223	0.5136	0.045*
C22	0.94211 (19)	0.98455 (15)	0.36645 (10)	0.0216 (3)
C23	1.1223 (2)	1.04052 (15)	0.40176 (10)	0.0219 (3)
C24	1.2294 (2)	0.96115 (16)	0.43134 (11)	0.0264 (3)
H24	1.3508	0.9991	0.4523	0.032*
C25	1.1585 (2)	0.82932 (17)	0.42985 (12)	0.0290 (4)
H25	1.2308	0.7756	0.4499	0.035*
C26	0.9798 (2)	0.77316 (16)	0.39892 (12)	0.0280 (4)
H26	0.9308	0.6823	0.4006	0.034*
C27	0.8751 (2)	0.84764 (15)	0.36628 (11)	0.0243 (3)
H27	0.7551	0.8067	0.343	0.029*
N1	-0.17163 (19)	0.91167 (18)	0.11094 (11)	0.0405 (4)
N2	1.19082 (16)	1.17505 (13)	0.40782 (9)	0.0235 (3)
O1	0.34481 (16)	0.55102 (12)	0.39676 (8)	0.0347 (3)
O2	0.48631 (16)	0.45316 (13)	0.28231 (9)	0.0391 (3)
O3	0.46894 (16)	0.67913 (13)	0.28613 (11)	0.0452 (4)
S1	0.38860 (5)	0.54905 (4)	0.30368 (3)	0.02578 (14)
O4	0.76791 (17)	0.45303 (13)	0.42219 (11)	0.0367 (3)
H10	0.673 (3)	0.457 (2)	0.3841 (18)	0.058 (7)*
H2O	0.740 (3)	0.450 (2)	0.4763 (17)	0.043 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0200 (7)	0.0216 (7)	0.0291 (8)	0.0037 (6)	0.0026 (6)	0.0065 (6)
C2	0.0259 (8)	0.0303 (9)	0.0300 (9)	0.0077 (6)	0.0049 (7)	0.0026 (7)
C3	0.0210 (8)	0.0374 (9)	0.0403 (10)	0.0086 (7)	0.0064 (7)	0.0111 (8)
C4	0.0263 (9)	0.0379 (10)	0.0363 (10)	0.0064 (7)	-0.0029 (7)	0.0085 (8)
C5	0.0372 (10)	0.0642 (13)	0.0260 (9)	0.0189 (9)	-0.0026 (8)	-0.0026 (9)
C6	0.0268 (9)	0.0564 (12)	0.0287 (9)	0.0164 (8)	0.0062 (7)	0.0061 (8)
C7	0.0310 (10)	0.0609 (14)	0.0530 (13)	0.0075 (9)	-0.0131 (9)	0.0063 (10)
C8	0.0304 (10)	0.0841 (16)	0.0351 (10)	0.0246 (10)	0.0014 (8)	0.0144 (10)
C9	0.0243 (9)	0.0614 (13)	0.0407 (11)	0.0043 (8)	0.0002 (8)	-0.0086 (9)
C10	0.0230 (8)	0.0478 (11)	0.0214 (8)	0.0107 (7)	0.0038 (6)	0.0016 (7)
C11	0.0295 (9)	0.0433 (10)	0.0291 (9)	0.0176 (8)	0.0046 (7)	0.0073 (7)
C12	0.0283 (9)	0.0329 (9)	0.0288 (9)	0.0098 (7)	0.0061 (7)	0.0044 (7)
C13	0.0215 (8)	0.0324 (9)	0.0236 (8)	0.0074 (6)	0.0051 (6)	0.0029 (7)

C14	0.0232 (8)	0.0324 (9)	0.0246 (8)	0.0085 (6)	0.0032 (6)	0.0019 (7)
C15	0.0233 (8)	0.0369 (9)	0.0246 (8)	0.0051 (7)	0.0036 (6)	0.0003 (7)
C16	0.0230 (8)	0.0263 (8)	0.0250 (8)	0.0049 (6)	0.0056 (6)	0.0022 (6)
C17	0.0208 (8)	0.0247 (8)	0.0259 (8)	0.0037 (6)	0.0040 (6)	0.0018 (6)
C18	0.0206 (7)	0.0238 (8)	0.0218 (7)	0.0038 (6)	0.0050 (6)	0.0017 (6)
C19	0.0256 (8)	0.0235 (8)	0.0305 (9)	0.0062 (6)	0.0033 (7)	0.0054 (7)
C20	0.0271 (8)	0.0204 (8)	0.0289 (8)	0.0029 (6)	0.0056 (6)	0.0047 (6)
C21	0.0194 (8)	0.0303 (9)	0.0335 (9)	-0.0007 (6)	-0.0001 (7)	0.0018 (7)
C22	0.0221 (7)	0.0211 (7)	0.0202 (7)	0.0035 (6)	0.0056 (6)	0.0008 (6)
C23	0.0218 (7)	0.0225 (8)	0.0201 (7)	0.0037 (6)	0.0051 (6)	0.0015 (6)
C24	0.0229 (8)	0.0291 (8)	0.0266 (8)	0.0076 (6)	0.0033 (6)	0.0027 (6)
C25	0.0312 (9)	0.0287 (8)	0.0303 (9)	0.0134 (7)	0.0061 (7)	0.0050 (7)
C26	0.0315 (9)	0.0226 (8)	0.0307 (9)	0.0072 (6)	0.0103 (7)	0.0024 (7)
C27	0.0237 (8)	0.0221 (8)	0.0249 (8)	0.0030 (6)	0.0066 (6)	0.0005 (6)
N1	0.0213 (7)	0.0603 (11)	0.0371 (9)	0.0114 (7)	-0.0014 (6)	0.0044 (8)
N2	0.0196 (6)	0.0229 (7)	0.0240 (7)	0.0006 (5)	0.0022 (5)	0.0012 (5)
O1	0.0312 (7)	0.0368 (7)	0.0277 (6)	0.0002 (5)	-0.0011 (5)	-0.0009 (5)
O2	0.0274 (6)	0.0419 (7)	0.0451 (8)	0.0168 (5)	-0.0062 (5)	-0.0039 (6)
O3	0.0298 (7)	0.0310 (7)	0.0664 (9)	-0.0075 (5)	-0.0052 (6)	0.0215 (6)
S1	0.0194 (2)	0.0226 (2)	0.0321 (2)	0.00188 (14)	-0.00032 (15)	0.00509 (16)
O4	0.0290 (7)	0.0443 (8)	0.0389 (8)	0.0131 (6)	0.0054 (6)	0.0084 (6)

Geometric parameters (Å, °)

C1—C6	1.379 (3)	C14—H14	0.95
C1—C2	1.385 (2)	C15—H15	0.95
C1—S1	1.771 (2)	C16—C17	1.348 (2)
C2—C3	1.384 (3)	C16—H16	0.95
C2—H2	0.95	C17—C18	1.447 (2)
C3—C4	1.380 (3)	C17—H17	0.95
C3—H3	0.95	C18—C19	1.390 (2)
C4—C5	1.384 (3)	C18—C22	1.433 (2)
C4—C7	1.506 (3)	C19—C20	1.372 (2)
C5—C6	1.384 (3)	C19—H19	0.95
C5—H5	0.95	C20—N2	1.328 (2)
C6—H6	0.95	C20—H20	0.95
C7—H7A	0.98	C21—N2	1.473 (2)
C7—H7B	0.98	C21—H21A	0.98
C7—H7C	0.98	C21—H21B	0.98
C8—N1	1.453 (3)	C21—H21C	0.98
C8—H8A	0.98	C22—C27	1.414 (2)
C8—H8B	0.98	C22—C23	1.418 (2)
C8—H8C	0.98	C23—N2	1.379 (2)
C9—N1	1.444 (3)	C23—C24	1.405 (2)
C9—H9A	0.98	C24—C25	1.366 (2)
C9—H9B	0.98	C24—H24	0.95
C9—H9C	0.98	C25—C26	1.398 (3)
C10—N1	1.368 (2)	C25—H25	0.95

C10—C11	1.400 (3)	C26—C27	1.365 (2)
C10—C15	1.413 (3)	C26—H26	0.95
C11—C12	1.379 (3)	C27—H27	0.95
C11—H11	0.95	O1—S1	1.4540 (15)
C12—C13	1.399 (2)	O2—S1	1.4502 (15)
C12—H12	0.95	O3—S1	1.4419 (16)
C13—C14	1.404 (3)	O4—H10	0.90 (3)
C13—C16	1.447 (2)	O4—H2O	0.86 (2)
C14—C15	1.375 (2)		
C6—C1—C2	119.68 (16)	C10—C15—H15	119.4
C6—C1—S1	120.42 (13)	C17—C16—C13	127.15 (15)
C2—C1—S1	119.90 (13)	C17—C16—H16	116.4
C3—C2—C1	120.28 (17)	C13—C16—H16	116.4
C3—C2—H2	119.9	C16—C17—C18	124.17 (15)
C1—C2—H2	119.9	C16—C17—H17	117.9
C4—C3—C2	120.72 (17)	C18—C17—H17	117.9
C4—C3—H3	119.6	C19—C18—C22	116.75 (15)
C2—C3—H3	119.6	C19—C18—C17	121.72 (15)
C3—C4—C5	118.28 (16)	C22—C18—C17	121.53 (14)
C3—C4—C7	120.44 (18)	C20—C19—C18	120.79 (16)
C5—C4—C7	121.28 (19)	C20—C19—H19	119.6
C4—C5—C6	121.72 (18)	C18—C19—H19	119.6
C4—C5—H5	119.1	N2—C20—C19	122.84 (15)
C6—C5—H5	119.1	N2—C20—H20	118.6
C1—C6—C5	119.32 (17)	C19—C20—H20	118.6
C1—C6—H6	120.3	N2—C21—H21A	109.5
C5—C6—H6	120.3	N2—C21—H21B	109.5
C4—C7—H7A	109.5	H21A—C21—H21B	109.5
C4—C7—H7B	109.5	N2—C21—H21C	109.5
H7A—C7—H7B	109.5	H21A—C21—H21C	109.5
C4—C7—H7C	109.5	H21B—C21—H21C	109.5
H7A—C7—H7C	109.5	C27—C22—C23	117.05 (15)
H7B—C7—H7C	109.5	C27—C22—C18	122.72 (14)
N1—C8—H8A	109.5	C23—C22—C18	120.21 (14)
N1—C8—H8B	109.5	N2—C23—C24	120.25 (14)
H8A—C8—H8B	109.5	N2—C23—C22	118.87 (15)
N1—C8—H8C	109.5	C24—C23—C22	120.87 (15)
H8A—C8—H8C	109.5	C25—C24—C23	119.84 (15)
H8B—C8—H8C	109.5	C25—C24—H24	120.1
N1—C9—H9A	109.5	C23—C24—H24	120.1
N1—C9—H9B	109.5	C24—C25—C26	120.22 (16)
H9A—C9—H9B	109.5	C24—C25—H25	119.9
N1—C9—H9C	109.5	C26—C25—H25	119.9
H9A—C9—H9C	109.5	C27—C26—C25	120.68 (15)
H9B—C9—H9C	109.5	C27—C26—H26	119.7
N1—C10—C11	120.83 (17)	C25—C26—H26	119.7
N1—C10—C15	121.65 (17)	C26—C27—C22	121.24 (15)

C11—C10—C15	117.51 (16)	C26—C27—H27	119.4
C12—C11—C10	120.62 (17)	C22—C27—H27	119.4
C12—C11—H11	119.7	C10—N1—C9	121.38 (17)
C10—C11—H11	119.7	C10—N1—C8	120.21 (18)
C11—C12—C13	122.12 (17)	C9—N1—C8	117.97 (17)
C11—C12—H12	118.9	C20—N2—C23	120.50 (14)
C13—C12—H12	118.9	C20—N2—C21	118.80 (14)
C12—C13—C14	117.18 (15)	C23—N2—C21	120.61 (14)
C12—C13—C16	119.35 (16)	O3—S1—O2	113.25 (10)
C14—C13—C16	123.45 (16)	O3—S1—O1	113.06 (10)
C15—C14—C13	121.21 (16)	O2—S1—O1	111.98 (9)
C15—C14—H14	119.4	O3—S1—C1	106.47 (9)
C13—C14—H14	119.4	O2—S1—C1	105.80 (9)
C14—C15—C10	121.29 (17)	O1—S1—C1	105.52 (9)
C14—C15—H15	119.4	H10—O4—H2O	107 (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>
O4—H2O...O1 ⁱ	0.86 (2)	2.07 (2)	2.922 (3)	175 (2)
O4—H10...O2	0.89 (2)	1.95 (3)	2.838 (3)	169 (2)
C14—H14...O3	0.95	2.41	3.359 (3)	174
C17—H17...O3	0.95	2.49	3.435 (3)	175
C27—H27...O3	0.95	2.34	3.282 (3)	172
C3—H3...O2 ⁱⁱ	0.95	2.59	3.535 (3)	171
C20—H20...O1 ⁱⁱⁱ	0.95	2.37	3.290 (3)	162

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