

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

4-{2-[4-(Dimethylamino)phenyl]ethenyl}-1-methylpyridinium 2,4,6-trimethylbenzenesulfonate monohydrate

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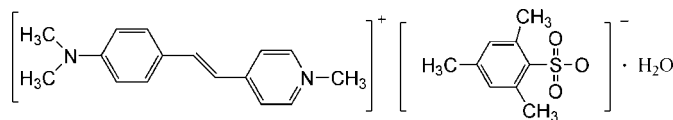
Received 25 January 2011; accepted 1 March 2011

Key indicators: single-crystal X-ray study; $T = 103$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.042; wR factor = 0.108; data-to-parameter ratio = 17.3.

In the crystal structure of the title organic salt, $\text{C}_{16}\text{H}_{19}\text{N}_2^{+}\cdot\text{C}_9\text{H}_{11}\text{O}_3\text{S}^{-}\cdot\text{H}_2\text{O}$, the cations pack head-to-tail within a sheet and are aligned in opposite directions in neighboring sheets. The benzene ring of the anion makes an angle of $76.99(6)^\circ$ with the plane of the cationic chromophore. The cations are situated in the ab plane, whereas the benzene rings of the anions lie in the ac plane.

Related literature

For the crystal structure of solvent-free 2,4,6-trimethylbenzenesulfonate (DSTMS), see: Yang *et al.* (2007); Mutter *et al.* (2007). For the crystal structure of 4-*N,N*-dimethylamino-4'-*N'*-methylstilbazolium tosylate (DAST) and DAST·H₂O, see: Marder *et al.* (1989); Pan *et al.* (1996); Bryant *et al.* (1993). For the synthesis, see: Marder *et al.* (1994).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{19}\text{N}_2^{+}\cdot\text{C}_9\text{H}_{11}\text{O}_3\text{S}^{-}\cdot\text{H}_2\text{O}$ $M_r = 456.59$

Triclinic, $P\bar{1}$
 $a = 8.1993(17)$ Å
 $b = 9.669(2)$ Å
 $c = 15.247(3)$ Å
 $\alpha = 87.806(7)^\circ$
 $\beta = 75.805(6)^\circ$
 $\gamma = 83.239(5)^\circ$

$V = 1163.7(4)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.17$ mm⁻¹
 $T = 103$ K
 $0.50 \times 0.40 \times 0.20$ mm

Data collection

Rigaku AFC10/Saturn724+ diffractometer
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.918$, $T_{\max} = 0.966$

11232 measured reflections
 5240 independent reflections
 4259 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.108$
 $S = 1.00$
 5240 reflections
 303 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.70$ e Å⁻³
 $\Delta\rho_{\min} = -0.35$ e Å⁻³

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *SHELXL97*.

The authors thank Professor Kaibei Yu, State Key Laboratory of Explosion Science and Technology of Beijing Institute of Technology, for the data collection. This work was supported by the National Basic Research Project of China (No. 2010CB630701).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2263).

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supplementary materials

Acta Cryst. (2011). E67, o823 [doi:10.1107/S1600536811007690]

4-{2-[4-(Dimethylamino)phenyl]ethenyl}-1-methylpyridinium 2,4,6-trimethylbenzenesulfonate monohydrate

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Comment

N,N-Dimethyl-4-[2-(1'-methylpyridinium-4'-yl)-vinyl]-phenyl-amine 2,4,6-trimethylbenzenesulfonate (DSTMS) is an organic nonlinear optical crystal, which is similar to 4-*N,N*-dimethylamino-4'-*N'*-methyl-stilbazolium tosylate (DAST). Both compounds show large nonlinear optical susceptibilities (Yang *et al.*, 2007; Marder *et al.*, 1989; Pan *et al.*, 1996; Mutter *et al.*, 2007). In the presence of water, orange DSTMS hydrate with no nonlinear optical effect is easy to obtain. Fig. 1 illustrates the molecular structure of DSTMS.H₂O together with the atomic numbering scheme. The C—H distances for the methyl groups are 0.98 Å, other H atoms are placed in idealized positions and constrained to have C—H=0.95 Å. The C—C distances for the phenyl groups range between 1.347 Å and 1.412 Å.

The unit cell of DSTMS.H₂O contains two (C₁₆H₁₉N₂)⁺ cations, two (C₉H₁₁O₃S)⁻ anions and two water molecules, with $\bar{1}$ symmetry. By comparing the data of geometric parameters of solvent free DSTMS and the hydrate, there are no obvious changes of bond distances and bond angles. In both compounds, the cations group pack head to tail within a sheet and are aligned in the opposite direction in the neighboring sheets. The phenyl rings in the anion group of DSTMS.H₂O lie at an angle of 76.99 (6)° relative to the cation chromophores, whereas the angle in the solvent free structure of DSTMS is 63.7 (2)°.

The crystal structure of DSTMS.H₂O (Fig. 2) is analogous to DAST.H₂O both belonging to triclinic space group *PT* (Bryant *et al.*, 1993). DSTMS.H₂O has two more methyl groups at the phenyl ring of the anion and the volume of unit cell therefore is larger compared with DAST.H₂O.

Experimental

DSTMS was synthesized by the condensation of 4-methyl-*N*-methyl pyridinium 2,4,6-trimethyl benzenesulfonate, which was prepared from 4-picoline and 2,4,6-trimethyl toluenesulfonate, and 4-*N,N*-dimethylamino-benzaldehyde in the presence of piperidine (Marder *et al.*, 1994). A crystal of DSTMS.H₂O was grown by slow evaporation at room temperature from a saturated solution of DSTMS and 90% methanol/water.

Refinement

H atoms of water were localized from Fourier maps and refined isotropically. Other H atoms were placed in calculated positions (C—H = 0.95–0.98 Å) and included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

Figures

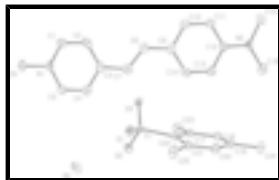


Fig. 1. Thermal-ellipsoid (50% probability) plot showing the atomic numbering scheme.

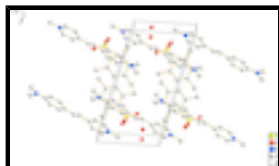


Fig. 2. Molecular packing plot of DSTMS.H₂O.

4-{2-[4-(Dimethylamino)phenyl]ethenyl}-1-methylpyridinium 2,4,6-trimethylbenzenesulfonate monohydrate

Crystal data

C₁₆H₁₉N₂⁺·C₉H₁₁O₃S⁻·H₂O

M_r = 456.59

Triclinic, *P*1̄

Hall symbol: -P 1

a = 8.1993 (17) Å

b = 9.669 (2) Å

c = 15.247 (3) Å

α = 87.806 (7)°

β = 75.805 (6)°

γ = 83.239 (5)°

V = 1163.7 (4) Å³

Z = 2

F(000) = 488

D_x = 1.303 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3579 reflections

θ = 3.2–27.5°

μ = 0.17 mm⁻¹

T = 103 K

Chunk, red

0.50 × 0.40 × 0.20 mm

Data collection

Rigaku AFC10/Saturn724+
diffractometer

Radiation source: Rotating Anode
graphite

Detector resolution: 28.5714 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*ABSCOR*; Higashi, 1995)

T_{min} = 0.918, *T_{max}* = 0.966

11232 measured reflections

5240 independent reflections

4259 reflections with *I* > 2σ(*I*)

R_{int} = 0.022

θ_{max} = 27.5°, θ_{min} = 3.2°

h = -10→10

k = -11→12

l = -19→19

Refinement

Refinement on *F*²

Least-squares matrix: full

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

$$R[F^2 > 2\sigma(F^2)] = 0.042$$

$$wR(F^2) = 0.108$$

$$S = 1.00$$

5240 reflections

303 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.560P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$$

Special details

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.36608 (5)	0.78675 (4)	0.16984 (2)	0.01575 (11)
O1	0.51685 (14)	0.75321 (13)	0.20319 (8)	0.0232 (3)
O2	0.36736 (15)	0.92045 (12)	0.12167 (8)	0.0231 (3)
O3	0.33464 (15)	0.67560 (12)	0.11702 (8)	0.0235 (3)
N1	1.13709 (16)	0.36393 (14)	0.06835 (9)	0.0163 (3)
N2	-0.18615 (17)	0.31865 (14)	0.36790 (9)	0.0199 (3)
C1	1.0477 (2)	0.25780 (17)	0.06110 (11)	0.0194 (3)
H1	1.1037	0.1764	0.0292	0.023*
C2	0.8769 (2)	0.26638 (18)	0.09932 (11)	0.0215 (3)
H2	0.8158	0.1908	0.0940	0.026*
C3	0.7916 (2)	0.38704 (18)	0.14644 (11)	0.0204 (3)
C4	0.8883 (2)	0.49457 (18)	0.15010 (11)	0.0221 (3)
H4	0.8351	0.5788	0.1794	0.027*
C5	1.0588 (2)	0.48092 (17)	0.11214 (11)	0.0197 (3)
H5	1.1228	0.5549	0.1167	0.024*
C6	1.3204 (2)	0.35286 (19)	0.02549 (11)	0.0226 (4)
H6A	1.3378	0.3588	-0.0404	0.027*
H6B	1.3750	0.2634	0.0421	0.027*
H6C	1.3701	0.4290	0.0463	0.027*
C7	0.6116 (2)	0.40354 (18)	0.19219 (11)	0.0222 (3)
H7	0.5612	0.4933	0.2138	0.027*
C8	0.5143 (2)	0.29984 (17)	0.20536 (11)	0.0209 (3)
H8	0.5658	0.2119	0.1810	0.025*

supplementary materials

C9	0.3364 (2)	0.30837 (18)	0.25350 (11)	0.0204 (3)
C10	0.2517 (2)	0.19128 (18)	0.25496 (11)	0.0213 (3)
H10	0.3134	0.1078	0.2282	0.026*
C11	0.0816 (2)	0.19291 (17)	0.29396 (10)	0.0189 (3)
H11	0.0281	0.1110	0.2939	0.023*
C12	-0.01440 (19)	0.31519 (16)	0.33420 (10)	0.0163 (3)
C13	0.0716 (2)	0.43197 (16)	0.33729 (11)	0.0202 (3)
H13	0.0117	0.5140	0.3670	0.024*
C14	0.2427 (2)	0.42795 (17)	0.29738 (11)	0.0213 (3)
H14	0.2983	0.5081	0.2997	0.026*
C15	-0.2692 (2)	0.19605 (18)	0.36304 (11)	0.0221 (3)
H15A	-0.2441	0.1659	0.3000	0.027*
H15B	-0.3918	0.2181	0.3858	0.027*
H15C	-0.2279	0.1212	0.4000	0.027*
C16	-0.2850 (2)	0.44394 (19)	0.40913 (13)	0.0295 (4)
H16A	-0.2528	0.4623	0.4650	0.035*
H16B	-0.4056	0.4316	0.4231	0.035*
H16C	-0.2634	0.5227	0.3671	0.035*
C17	0.02360 (19)	0.82889 (15)	0.24753 (10)	0.0154 (3)
C18	-0.1177 (2)	0.83123 (16)	0.32025 (11)	0.0174 (3)
H18	-0.2270	0.8412	0.3084	0.021*
C19	-0.1047 (2)	0.81959 (16)	0.40931 (11)	0.0183 (3)
C20	0.0562 (2)	0.80729 (17)	0.42491 (11)	0.0199 (3)
H20	0.0670	0.8027	0.4856	0.024*
C21	0.2030 (2)	0.80140 (16)	0.35469 (10)	0.0178 (3)
C22	0.18631 (19)	0.80801 (15)	0.26519 (10)	0.0143 (3)
C23	-0.0066 (2)	0.85704 (17)	0.15439 (11)	0.0211 (3)
H23A	-0.1263	0.8522	0.1567	0.025*
H23B	0.0635	0.7872	0.1122	0.025*
H23C	0.0233	0.9500	0.1338	0.025*
C24	-0.2586 (2)	0.8222 (2)	0.48747 (11)	0.0261 (4)
H24A	-0.3611	0.8382	0.4646	0.031*
H24B	-0.2578	0.8972	0.5287	0.031*
H24C	-0.2570	0.7327	0.5199	0.031*
C25	0.3698 (2)	0.7919 (2)	0.38181 (12)	0.0287 (4)
H25A	0.3481	0.8006	0.4476	0.034*
H25B	0.4343	0.8671	0.3521	0.034*
H25C	0.4350	0.7017	0.3632	0.034*
O4	0.69606 (17)	1.00845 (14)	0.04707 (10)	0.0259 (3)
H4A	0.611 (3)	0.977 (3)	0.0748 (18)	0.053 (8)*
H4B	0.675 (3)	1.039 (3)	-0.0023 (18)	0.050 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01557 (19)	0.01519 (19)	0.01466 (18)	-0.00387 (14)	0.00108 (14)	-0.00183 (13)
O1	0.0144 (5)	0.0307 (7)	0.0228 (6)	-0.0005 (5)	-0.0015 (5)	-0.0032 (5)
O2	0.0271 (6)	0.0198 (6)	0.0196 (6)	-0.0058 (5)	0.0006 (5)	0.0033 (4)

O3	0.0215 (6)	0.0238 (6)	0.0230 (6)	-0.0079 (5)	0.0028 (5)	-0.0095 (5)
N1	0.0142 (6)	0.0215 (7)	0.0136 (6)	-0.0040 (5)	-0.0028 (5)	0.0006 (5)
N2	0.0143 (6)	0.0190 (7)	0.0240 (7)	-0.0016 (5)	0.0001 (5)	-0.0006 (5)
C1	0.0218 (8)	0.0198 (8)	0.0186 (8)	-0.0046 (6)	-0.0077 (6)	0.0004 (6)
C2	0.0218 (8)	0.0247 (8)	0.0217 (8)	-0.0100 (7)	-0.0098 (7)	0.0048 (6)
C3	0.0183 (8)	0.0276 (9)	0.0160 (7)	-0.0042 (7)	-0.0058 (6)	0.0073 (6)
C4	0.0212 (8)	0.0242 (8)	0.0198 (8)	-0.0014 (7)	-0.0031 (6)	0.0000 (6)
C5	0.0205 (8)	0.0207 (8)	0.0179 (8)	-0.0056 (6)	-0.0033 (6)	-0.0005 (6)
C6	0.0136 (7)	0.0326 (9)	0.0202 (8)	-0.0046 (7)	-0.0002 (6)	-0.0015 (7)
C7	0.0229 (8)	0.0219 (8)	0.0219 (8)	-0.0007 (7)	-0.0064 (7)	0.0010 (6)
C8	0.0200 (8)	0.0229 (8)	0.0202 (8)	-0.0011 (6)	-0.0061 (6)	0.0006 (6)
C9	0.0163 (8)	0.0277 (9)	0.0164 (7)	0.0005 (6)	-0.0041 (6)	0.0034 (6)
C10	0.0198 (8)	0.0236 (8)	0.0190 (8)	0.0026 (6)	-0.0042 (6)	-0.0025 (6)
C11	0.0203 (8)	0.0175 (8)	0.0186 (8)	-0.0010 (6)	-0.0045 (6)	-0.0016 (6)
C12	0.0159 (7)	0.0176 (7)	0.0146 (7)	-0.0010 (6)	-0.0029 (6)	0.0021 (6)
C13	0.0190 (8)	0.0157 (7)	0.0248 (8)	0.0005 (6)	-0.0046 (6)	0.0002 (6)
C14	0.0213 (8)	0.0187 (8)	0.0255 (8)	-0.0057 (6)	-0.0078 (7)	0.0048 (6)
C15	0.0199 (8)	0.0244 (8)	0.0222 (8)	-0.0057 (7)	-0.0046 (6)	0.0039 (6)
C16	0.0182 (8)	0.0279 (9)	0.0363 (10)	0.0028 (7)	0.0034 (7)	-0.0055 (8)
C17	0.0176 (7)	0.0116 (7)	0.0167 (7)	-0.0005 (6)	-0.0043 (6)	0.0004 (5)
C18	0.0151 (7)	0.0165 (7)	0.0204 (8)	-0.0010 (6)	-0.0042 (6)	-0.0005 (6)
C19	0.0170 (8)	0.0173 (8)	0.0181 (7)	-0.0018 (6)	0.0001 (6)	0.0007 (6)
C20	0.0197 (8)	0.0262 (8)	0.0132 (7)	-0.0023 (7)	-0.0027 (6)	0.0006 (6)
C21	0.0159 (7)	0.0196 (8)	0.0179 (7)	-0.0021 (6)	-0.0040 (6)	-0.0004 (6)
C22	0.0146 (7)	0.0115 (7)	0.0151 (7)	-0.0020 (5)	0.0005 (6)	-0.0014 (5)
C23	0.0228 (8)	0.0232 (8)	0.0180 (8)	-0.0004 (7)	-0.0074 (6)	0.0015 (6)
C24	0.0193 (8)	0.0344 (10)	0.0201 (8)	-0.0005 (7)	0.0025 (7)	0.0008 (7)
C25	0.0191 (8)	0.0506 (12)	0.0169 (8)	-0.0021 (8)	-0.0058 (7)	-0.0031 (8)
O4	0.0243 (7)	0.0278 (7)	0.0286 (7)	-0.0110 (5)	-0.0098 (6)	0.0085 (5)

Geometric parameters (Å, °)

S1—O1	1.4468 (12)	C12—C13	1.408 (2)
S1—O3	1.4503 (11)	C13—C14	1.382 (2)
S1—O2	1.4619 (12)	C13—H13	0.9500
S1—C22	1.7969 (15)	C14—H14	0.9500
N1—C5	1.347 (2)	C15—H15A	0.9800
N1—C1	1.352 (2)	C15—H15B	0.9800
N1—C6	1.478 (2)	C15—H15C	0.9800
N2—C12	1.372 (2)	C16—H16A	0.9800
N2—C15	1.448 (2)	C16—H16B	0.9800
N2—C16	1.448 (2)	C16—H16C	0.9800
C1—C2	1.372 (2)	C17—C18	1.392 (2)
C1—H1	0.9500	C17—C22	1.415 (2)
C2—C3	1.411 (2)	C17—C23	1.510 (2)
C2—H2	0.9500	C18—C19	1.387 (2)
C3—C4	1.390 (2)	C18—H18	0.9500
C3—C7	1.463 (2)	C19—C20	1.388 (2)
C4—C5	1.369 (2)	C19—C24	1.507 (2)

supplementary materials

C4—H4	0.9500	C20—C21	1.398 (2)
C5—H5	0.9500	C20—H20	0.9500
C6—H6A	0.9800	C21—C22	1.403 (2)
C6—H6B	0.9800	C21—C25	1.515 (2)
C6—H6C	0.9800	C23—H23A	0.9800
C7—C8	1.333 (2)	C23—H23B	0.9800
C7—H7	0.9500	C23—H23C	0.9800
C8—C9	1.457 (2)	C24—H24A	0.9800
C8—H8	0.9500	C24—H24B	0.9800
C9—C10	1.393 (2)	C24—H24C	0.9800
C9—C14	1.405 (2)	C25—H25A	0.9800
C10—C11	1.374 (2)	C25—H25B	0.9800
C10—H10	0.9500	C25—H25C	0.9800
C11—C12	1.412 (2)	O4—H4A	0.81 (3)
C11—H11	0.9500	O4—H4B	0.85 (3)
O1—S1—O3	112.80 (7)	C12—C13—H13	119.8
O1—S1—O2	111.61 (7)	C13—C14—C9	121.66 (15)
O3—S1—O2	112.36 (7)	C13—C14—H14	119.2
O1—S1—C22	108.39 (7)	C9—C14—H14	119.2
O3—S1—C22	105.54 (7)	N2—C15—H15A	109.5
O2—S1—C22	105.59 (7)	N2—C15—H15B	109.5
C5—N1—C1	120.26 (14)	H15A—C15—H15B	109.5
C5—N1—C6	120.03 (13)	N2—C15—H15C	109.5
C1—N1—C6	119.69 (13)	H15A—C15—H15C	109.5
C12—N2—C15	119.93 (13)	H15B—C15—H15C	109.5
C12—N2—C16	120.42 (14)	N2—C16—H16A	109.5
C15—N2—C16	119.65 (14)	N2—C16—H16B	109.5
N1—C1—C2	120.76 (15)	H16A—C16—H16B	109.5
N1—C1—H1	119.6	N2—C16—H16C	109.5
C2—C1—H1	119.6	H16A—C16—H16C	109.5
C1—C2—C3	120.28 (15)	H16B—C16—H16C	109.5
C1—C2—H2	119.9	C18—C17—C22	118.60 (14)
C3—C2—H2	119.9	C18—C17—C23	117.57 (14)
C4—C3—C2	116.78 (15)	C22—C17—C23	123.74 (14)
C4—C3—C7	119.04 (15)	C19—C18—C17	122.41 (15)
C2—C3—C7	124.16 (15)	C19—C18—H18	118.8
C5—C4—C3	121.03 (16)	C17—C18—H18	118.8
C5—C4—H4	119.5	C18—C19—C20	117.74 (14)
C3—C4—H4	119.5	C18—C19—C24	121.92 (15)
N1—C5—C4	120.85 (15)	C20—C19—C24	120.33 (15)
N1—C5—H5	119.6	C19—C20—C21	122.50 (15)
C4—C5—H5	119.6	C19—C20—H20	118.7
N1—C6—H6A	109.5	C21—C20—H20	118.7
N1—C6—H6B	109.5	C20—C21—C22	118.52 (14)
H6A—C6—H6B	109.5	C20—C21—C25	116.73 (14)
N1—C6—H6C	109.5	C22—C21—C25	124.74 (14)
H6A—C6—H6C	109.5	C21—C22—C17	120.04 (14)
H6B—C6—H6C	109.5	C21—C22—S1	122.28 (12)
C8—C7—C3	123.74 (16)	C17—C22—S1	117.66 (11)

C8—C7—H7	118.1	C17—C23—H23A	109.5
C3—C7—H7	118.1	C17—C23—H23B	109.5
C7—C8—C9	126.30 (16)	H23A—C23—H23B	109.5
C7—C8—H8	116.9	C17—C23—H23C	109.5
C9—C8—H8	116.8	H23A—C23—H23C	109.5
C10—C9—C14	117.34 (15)	H23B—C23—H23C	109.5
C10—C9—C8	118.18 (15)	C19—C24—H24A	109.5
C14—C9—C8	124.46 (16)	C19—C24—H24B	109.5
C11—C10—C9	121.99 (15)	H24A—C24—H24B	109.5
C11—C10—H10	119.0	C19—C24—H24C	109.5
C9—C10—H10	119.0	H24A—C24—H24C	109.5
C10—C11—C12	120.65 (15)	H24B—C24—H24C	109.5
C10—C11—H11	119.7	C21—C25—H25A	109.5
C12—C11—H11	119.7	C21—C25—H25B	109.5
N2—C12—C13	121.89 (14)	H25A—C25—H25B	109.5
N2—C12—C11	120.30 (14)	C21—C25—H25C	109.5
C13—C12—C11	117.81 (14)	H25A—C25—H25C	109.5
C14—C13—C12	120.40 (15)	H25B—C25—H25C	109.5
C14—C13—H13	119.8	H4A—O4—H4B	105 (2)
C5—N1—C1—C2	-1.1 (2)	C12—C13—C14—C9	-0.6 (2)
C6—N1—C1—C2	-179.16 (14)	C10—C9—C14—C13	-2.6 (2)
N1—C1—C2—C3	0.4 (2)	C8—C9—C14—C13	176.07 (15)
C1—C2—C3—C4	1.1 (2)	C22—C17—C18—C19	2.7 (2)
C1—C2—C3—C7	-177.60 (15)	C23—C17—C18—C19	-173.92 (14)
C2—C3—C4—C5	-2.1 (2)	C17—C18—C19—C20	1.0 (2)
C7—C3—C4—C5	176.71 (15)	C17—C18—C19—C24	-179.96 (15)
C1—N1—C5—C4	0.1 (2)	C18—C19—C20—C21	-2.3 (2)
C6—N1—C5—C4	178.19 (15)	C24—C19—C20—C21	178.59 (15)
C3—C4—C5—N1	1.5 (3)	C19—C20—C21—C22	-0.1 (2)
C4—C3—C7—C8	-168.78 (16)	C19—C20—C21—C25	178.41 (16)
C2—C3—C7—C8	9.9 (3)	C20—C21—C22—C17	3.9 (2)
C3—C7—C8—C9	177.35 (15)	C25—C21—C22—C17	-174.51 (15)
C7—C8—C9—C10	175.50 (16)	C20—C21—C22—S1	-174.67 (12)
C7—C8—C9—C14	-3.2 (3)	C25—C21—C22—S1	7.0 (2)
C14—C9—C10—C11	2.8 (2)	C18—C17—C22—C21	-5.1 (2)
C8—C9—C10—C11	-175.95 (15)	C23—C17—C22—C21	171.28 (14)
C9—C10—C11—C12	0.2 (2)	C18—C17—C22—S1	173.46 (11)
C15—N2—C12—C13	179.87 (15)	C23—C17—C22—S1	-10.1 (2)
C16—N2—C12—C13	-0.7 (2)	O1—S1—C22—C21	4.19 (15)
C15—N2—C12—C11	0.6 (2)	O3—S1—C22—C21	125.28 (13)
C16—N2—C12—C11	-179.95 (15)	O2—S1—C22—C21	-115.53 (13)
C10—C11—C12—N2	175.85 (14)	O1—S1—C22—C17	-174.38 (11)
C10—C11—C12—C13	-3.4 (2)	O3—S1—C22—C17	-53.28 (13)
N2—C12—C13—C14	-175.66 (15)	O2—S1—C22—C17	65.90 (13)
C11—C12—C13—C14	3.6 (2)		

Fig. 1

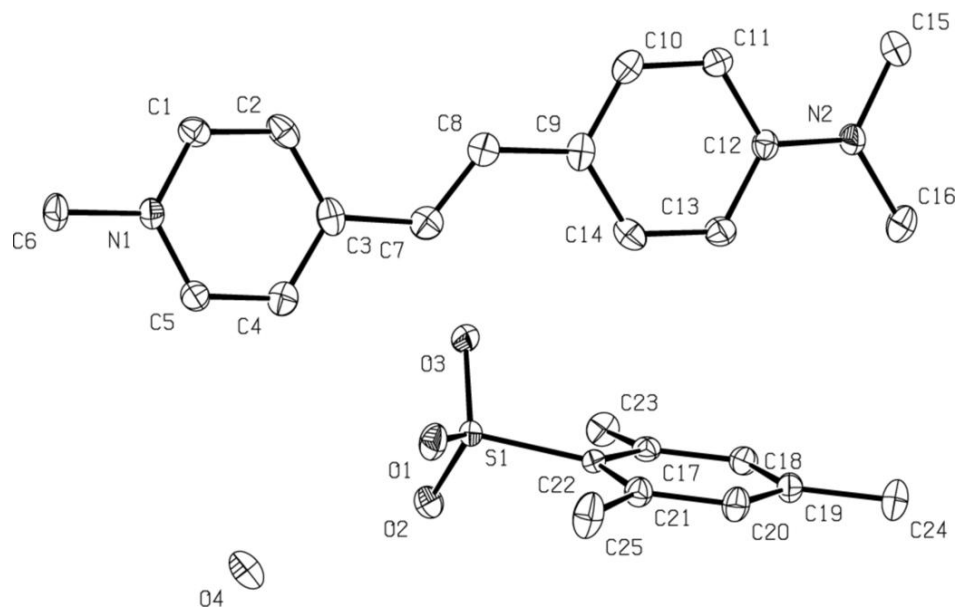


Fig. 2

