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Bis(triethylammonium) 4,4′-diamino-*trans*-stilbene-2,2′-disulfonate

Stéphane Dufresne, Michael Gaultois‡ and W. G. Skene*

Department of Chemistry, University of Montreal, CP 6128, succ. Centre-ville, Montréal, Québec, Canada H3C 3J7
Correspondence e-mail: w.skene@umontreal.ca

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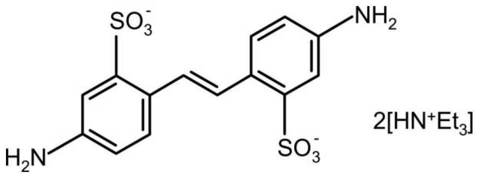
Key indicators: single-crystal X-ray study; T = 220 K; mean σ(C–C) = 0.004 Å; R factor = 0.052; wR factor = 0.150; data-to-parameter ratio = 16.6.

In the title compound, $2C_6H_{16}N^+\cdot C_{14}H_{12}N_2O_6S_2^{2-}$, the anion possesses a crystallographically imposed centre of symmetry. The stilbene group adopts an E configuration, and the two benzene rings are each twisted from its mean plane by 16.05 (10)°. The crystal packing exhibits N—H⋯O hydrogen bonds, which link the anions into two-dimensional layers parallel to the plane formed by the b+c and a vectors, with protruding (up and down) triethylammonium cations.

Related literature

For general background, see: Bischof *et al.* (2001); Bourgeaux & Skene (2007); Bourgeaux *et al.* (2007); Dufresne *et al.* (2007); Irie (2000); Momotake & Arai (2004); Pérez Guarìn *et al.* (2007). For related literature, see: Wang *et al.* (2005); Zhang *et al.* (2005).



Experimental

Crystal data

$2C_6H_{16}N^+\cdot C_{14}H_{12}N_2O_6S_2^{2-}$
M_r = 572.79
Triclinic, $P\bar{1}$
a = 8.5117 (4) Å
b = 8.5273 (4) Å
c = 12.0711 (5) Å
α = 103.330 (2)°
β = 103.243 (2)°
γ = 106.142 (3)°
V = 777.60 (6) Å^3
Z = 1
Cu $K\alpha$ radiation
μ = 1.91 mm^{-1}
T = 220 (2) K
0.29 × 0.21 × 0.19 mm

Data collection

Bruker SMART 2000 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.640, T_{max} = 0.696
8255 measured reflections
2930 independent reflections
2772 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.150
S = 1.08
2930 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯O1^{i}	0.87	2.17	2.946 (2)	149
N1—H1B⋯O3^{ii}	0.87	2.06	2.915 (2)	166
N2—H2⋯O2^{iii}	0.92	1.84	2.747 (2)	171

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $x+1, y, z$; (iii) $-x, -y+2, -z+1$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *UdMX* (Marris, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2287).

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‡ Current address: Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2.

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supplementary materials

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Bis(triethylammonium) 4,4'-diamino-*trans*-stilbene-2,2'-disulfonate

S. Dufresne, M. Gaultois and **W. G. Skene**

Comment

Stilbenes such as an anion (I) of the title compound are interesting compounds because of the conjugation arising between the two phenyl groups. As a result, these compounds can be excited with UV light to induce conversion between the *E* and *Z* isomers (Irie, 2000; Momotake & Arai, 2004). Stilbenes have found wide spread applications as photoactive switches (Irie, 2000) owing to the absorption differences of the two isomers allowing for selective excitation of either isomer. Compound (I) is of particular interest because the photoconversion between the two isomers is suppressed resulting in intense fluorescence. Consequently, it is used as a textile fluorescent brightener (Bischof *et al.*, 2001). Owing to our ongoing azomethine research with functional materials, (Bourgeaux *et al.*, 2007, Pérez Guarìn *et al.*, 2007, Dufresne *et al.*, 2007, Bourgeaux & Skene, 2007) compound (I) is an appealing monomer for the synthesis of novel water soluble conjugated polyazomethines because of its two aryl amino groups. X-ray crystallography of this monomer was pursued to unequivocally confirm the regio substitution of the primary amines, the geometry of the unsaturated bond, and cation exchange, all of which cannot be confirmed by conventional methods.

The salient features of (I) derived from the crystal structures are the regiospecific positions of the two sulfonic anions located in the 4, 4' positions and the *para* substitution of the primary amines on the stilbene. Cation exchange of the H atoms with triethylammonium cations was also confirmed. These are of importance because they cannot be unequivocally confirmed by NMR spectroscopy. The *E* isomer of the unsaturated bond was also verified.

The mean plane described by the two benzenes and that of the central alkene of (I) are twisted by 16.05 (10)°. This is in contrast to analogous stilbenes whose mean plane angles are considerably smaller, *i.e.*, 2.72 ° (Wang *et al.*, 2005) and 1.86 ° (Zhang *et al.*, 2005). Similarly, the bond distance of the central alkene is also different from other stilbenes. For example, the C7—C7^{i} bond length is 1.331 (4) Å compared to 1.317 Å and 1.316 Å for its unsubstituted analogue. Conversely, the C7—C6 bond distance (1.464 (2) Å) is comparable to that of its analogues that are 1.463 Å and 1.456 Å.

(I) forms a well defined three-dimensional network involving the ionic groups illustrated in Fig. 2. From this figure it is evident that the diaminostilbenes are distributed in parallel *bc* planes that are separated by 7.114 (16) Å. Similarly, the triethylammonium cations are located in different parallel planes. Each sulfonic anion coordinates to three triethylammonium cations. Two cations form a O···H—C bond with the sulfonic anion involving O3···H12B—C12 and O1···H10B—C10 with respective bond lengths of 2.438 (2) and 2.489 (2) Å and angles of 167 and 163 °. The third cation forms a hydrogen bond involving N2—H2···O2^{iv} (Figure 3). The combined interactions involving the ionic species are illustrated in Figure 4.

Hydrogen bonding (Table 1) also occurs between the sulfonic anion and the primary amine of two parallel molecules of (I). An additional intermolecular hydrogen bond takes place between the second sulfonic anion acceptor and the triethylammonium cation donor of two different molecules of (I). These interactions are represented in Fig. 3.

Experimental

4,4'-Diamino-2,2'-stilbene-disulfonic acid from Aldrich was purified by successive acid and base washes. The starting material was then dissolved in an aqueous solution of triethylamine. The desired product was precipitated from cold ethanol and then crystallized from ethyl acetate.

Refinement

H atoms were placed in calculated positions (C—H 0.93–0.97 Å, N—H 0.87–0.92 Å) and they were included in the riding-model refinement approximation, with $U_{\rm iso}$(H) = 1.2–1.5 $U_{\rm eq}$ of the parent atom.

Figures

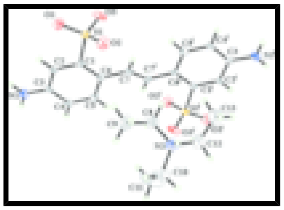


Fig. 1. *ORTEP* representation of (I) with the numbering scheme adopted (Farrugia, 1997). Ellipsoids drawn at 30% probability level. [Symmetry code: (i) −*x*, 1 − *y*, 1 − *z*.]

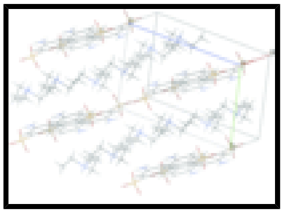


Fig. 2. The three-dimensional network demonstrating the well arranged layer assembly.

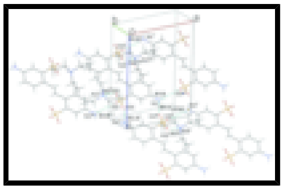


Fig. 3. Supramolecular structure showing the intermolecular hydrogen-bonding. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) −*x*, 1 − *y*, 1 − *z*; (ii) −*x* + 1, −*y* + 2, −*z* + 2; (iii) *x* + 1, *y*, *z*; (iv) −*x*, −*y* + 2, −*z* + 1; (v) 1 − *x*, 1 − *y*, 1 − *z*; (vi) 1 − *x*, 2 − *y*, 2 − *z*; (vii) *x* − 1, *y*, *z*; (viii) *x*, *y* − 1, *z*; (ix) 1 + *x*, *y*, 1 + *z*; (*x*) 2 − *x*, 2 − *y*, 2 − *z*.]

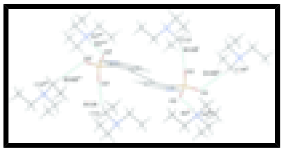


Fig. 4. Schematic representation of the sulfonate interactions with the triethylammonium cations. [Symmetry codes: (i) −*x*, 1 − *y*, 1 − *z*; (viii) *x*, *y* − 1, *z*; (xi) *x*, *y*, 1 + *z*; (xii) −*x*, 1 − *y*, −*z*.]

Bis(triethylammonium) 4,4'-diamino-*trans*-stilbene-2,2'-disulfonate

Crystal data

$2C_6H_{16}N^+\cdot C_{14}H_{12}N_2O_6S_2^{2-}$	$Z = 1$
$M_r = 572.79$	$F_{000} = 308$
Triclinic, $P\overline{1}$	$D_x = 1.219$ Mg m^{-3}
Hall symbol: -P 1	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å

a = 8.5117 (4) Å	Cell parameters from 6392 reflections
b = 8.5273 (4) Å	θ = 4.0–72.0º
c = 12.0711 (5) Å	μ = 1.91 mm^{-1}
α = 103.330 (2)º	T = 220 (2) K
β = 103.243 (2)º	Block, colourless
γ = 106.142 (3)º	0.29 × 0.21 × 0.19 mm
V = 777.60 (6) Å^3	

Data collection

Bruker SMART 2000 diffractometer	2930 independent reflections
Radiation source: X-ray Sealed Tube	2772 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\rm int}$ = 0.044
Detector resolution: 5.5 pixels mm^{-1}	$\theta_{\rm max}$ = 72.0º
T = 220(2) K	$\theta_{\rm min}$ = 4.0º
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -8 \rightarrow 9$
$T_{\rm min}$ = 0.640, $T_{\rm max}$ = 0.696	$l = -14 \rightarrow 14$
8255 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.2755P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.150	$(\Delta/\sigma)_{\rm max}$ = 0.001
S = 1.08	$\Delta\rho_{\rm max}$ = 0.54 e Å^{-3}
2930 reflections	$\Delta\rho_{\rm min}$ = −0.40 e Å^{-3}
176 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.019 (2)
Secondary atom site location: difference Fourier map	

Special details

Experimental. X-ray crystallographic data for I were collected from a single-crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker *SMART* 2 K Charged-Coupled Device (CCD) Area Detector using the program *SMART* and normal focus sealed tube source graphite monochromated Cu—Kα radiation. The crystal-to-detector distance was 4.908 cm, and the data collection was carried out in 512 *x* 512 pixel mode, utilizing 4 *x* 4 pixel binning. The initial unit-cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0 degree scan in 30 frames over four different parts of the reciprocal space (120 frames total). One complete sphere of data was collected, to better than 0.8Å resolution. Upon completion of the data collection, the first 101 frames were recollected in order to improve the decay correction analysis.

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 $F^2 > 2\mathrm{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
S1	0.11164 (5)	0.81398 (5)	0.80610 (4)	0.0280 (2)
O1	0.2049 (2)	0.9304 (2)	0.92526 (13)	0.0516 (5)
O2	0.0486 (2)	0.9013 (2)	0.72497 (14)	0.0445 (4)
O3	−0.0245 (2)	0.6634 (2)	0.80132 (17)	0.0494 (5)
N1	0.7007 (2)	0.7477 (2)	0.87894 (16)	0.0415 (4)
H1A	0.7263	0.8137	0.9520	0.050*
H1B	0.7749	0.7051	0.8575	0.050*
N2	0.0671 (3)	0.8267 (3)	0.23644 (19)	0.0463 (5)
H2	0.0294	0.9185	0.2417	0.056*
C1	0.2603 (2)	0.7335 (2)	0.75102 (15)	0.0242 (4)
C2	0.4227 (2)	0.7782 (2)	0.83059 (16)	0.0280 (4)
H2A	0.4523	0.8550	0.9080	0.034*
C3	0.5441 (2)	0.7109 (2)	0.79795 (16)	0.0291 (4)
C4	0.4967 (2)	0.6014 (3)	0.68024 (17)	0.0348 (4)
H4	0.5763	0.5569	0.6547	0.042*
C5	0.3343 (3)	0.5586 (3)	0.60167 (17)	0.0351 (4)
H5	0.3067	0.4852	0.5234	0.042*
C6	0.2085 (2)	0.6197 (2)	0.63331 (15)	0.0277 (4)
C7	0.0347 (2)	0.5670 (2)	0.54995 (15)	0.0307 (4)
H7	−0.0332	0.6330	0.5684	0.037*
C8	0.0904 (4)	0.7980 (4)	0.3540 (3)	0.0622 (7)
H8A	0.1335	0.7026	0.3532	0.075*
H8B	−0.0214	0.7651	0.3680	0.075*
C9	0.2148 (5)	0.9560 (5)	0.4557 (3)	0.0858 (11)
H9A	0.3288	0.9820	0.4468	0.129*
H9B	0.2186	0.9345	0.5316	0.129*
H9C	0.1767	1.0528	0.4538	0.129*
C10	0.2245 (5)	0.8729 (4)	0.2002 (3)	0.0729 (9)
H10A	0.3066	0.9830	0.2573	0.088*
H10B	0.1940	0.8890	0.1212	0.088*
C11	0.3116 (6)	0.7401 (6)	0.1942 (6)	0.130 (2)
H11A	0.3452	0.7256	0.2726	0.195*
H11B	0.4129	0.7782	0.1699	0.195*
H11C	0.2323	0.6313	0.1364	0.195*
C12	−0.0755 (4)	0.6737 (4)	0.1384 (3)	0.0648 (8)

H12A	−0.0741	0.6869	0.0600	0.078*
H12B	−0.0526	0.5681	0.1416	0.078*
C13	−0.2488 (4)	0.6566 (4)	0.1500 (3)	0.0773 (9)
H13A	−0.2557	0.6286	0.2226	0.116*
H13B	−0.3357	0.5656	0.0811	0.116*
H13C	−0.2684	0.7642	0.1537	0.116*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0284 (3)	0.0280 (3)	0.0336 (3)	0.0166 (2)	0.0152 (2)	0.00674 (19)
O1	0.0486 (9)	0.0658 (11)	0.0379 (8)	0.0347 (8)	0.0133 (7)	−0.0061 (7)
O2	0.0582 (9)	0.0408 (9)	0.0499 (9)	0.0359 (7)	0.0203 (7)	0.0164 (7)
O3	0.0405 (8)	0.0406 (9)	0.0872 (12)	0.0223 (7)	0.0430 (8)	0.0244 (8)
N1	0.0283 (8)	0.0525 (11)	0.0418 (9)	0.0206 (7)	0.0121 (7)	0.0023 (8)
N2	0.0646 (12)	0.0398 (10)	0.0619 (12)	0.0348 (9)	0.0345 (10)	0.0311 (9)
C1	0.0259 (8)	0.0232 (8)	0.0283 (8)	0.0116 (6)	0.0143 (7)	0.0077 (6)
C2	0.0276 (9)	0.0286 (9)	0.0288 (8)	0.0110 (7)	0.0135 (7)	0.0045 (6)
C3	0.0252 (8)	0.0313 (9)	0.0352 (9)	0.0118 (7)	0.0157 (7)	0.0098 (7)
C4	0.0332 (10)	0.0409 (11)	0.0370 (10)	0.0188 (8)	0.0212 (8)	0.0072 (8)
C5	0.0371 (10)	0.0423 (11)	0.0282 (9)	0.0183 (8)	0.0166 (8)	0.0037 (7)
C6	0.0310 (9)	0.0302 (9)	0.0257 (8)	0.0133 (7)	0.0134 (7)	0.0079 (7)
C7	0.0333 (9)	0.0336 (10)	0.0284 (9)	0.0163 (7)	0.0117 (7)	0.0081 (7)
C8	0.0701 (17)	0.0711 (19)	0.0644 (17)	0.0320 (15)	0.0279 (14)	0.0403 (14)
C9	0.086 (2)	0.102 (3)	0.068 (2)	0.029 (2)	0.0112 (17)	0.0407 (19)
C10	0.096 (2)	0.0607 (18)	0.106 (2)	0.0428 (16)	0.073 (2)	0.0467 (17)
C11	0.120 (4)	0.097 (3)	0.240 (7)	0.071 (3)	0.128 (4)	0.062 (4)
C12	0.089 (2)	0.0455 (15)	0.0626 (16)	0.0323 (14)	0.0167 (15)	0.0184 (12)
C13	0.076 (2)	0.0530 (17)	0.095 (2)	0.0094 (15)	0.0166 (18)	0.0346 (16)

Geometric parameters (Å, °)

S1—O1	1.4370 (15)	C7—C7^{i}	1.331 (4)
S1—O3	1.4502 (15)	C7—H7	0.94
S1—O2	1.4560 (15)	C8—C9	1.513 (5)
S1—C1	1.7814 (17)	C8—H8A	0.98
N1—C3	1.364 (2)	C8—H8B	0.98
N1—H1A	0.87	C9—H9A	0.97
N1—H1B	0.87	C9—H9B	0.97
N2—C8	1.474 (3)	C9—H9C	0.97
N2—C10	1.482 (3)	C10—C11	1.514 (5)
N2—C12	1.525 (4)	C10—H10A	0.98
N2—H2	0.92	C10—H10B	0.98
C1—C2	1.381 (2)	C11—H11A	0.97
C1—C6	1.412 (2)	C11—H11B	0.97
C2—C3	1.401 (2)	C11—H11C	0.97
C2—H2A	0.94	C12—C13	1.484 (5)
C3—C4	1.403 (3)	C12—H12A	0.98

C4—C5	1.379 (3)	C12—H12B	0.98
C4—H4	0.94	C13—H13A	0.97
C5—C6	1.403 (3)	C13—H13B	0.97
C5—H5	0.94	C13—H13C	0.97
C6—C7	1.464 (2)		

O1—S1—O3	113.87 (11)	N2—C8—C9	112.4 (2)
O1—S1—O2	111.88 (10)	N2—C8—H8A	109.1
O3—S1—O2	111.58 (10)	C9—C8—H8A	109.1
O1—S1—C1	106.96 (9)	N2—C8—H8B	109.1
O3—S1—C1	105.30 (8)	C9—C8—H8B	109.1
O2—S1—C1	106.64 (8)	H8A—C8—H8B	107.9
C3—N1—H1A	120	C8—C9—H9A	109.5
C3—N1—H1B	120	C8—C9—H9B	109.5
H1A—N1—H1B	120	H9A—C9—H9B	109.5
C8—N2—C10	115.9 (2)	C8—C9—H9C	109.5
C8—N2—C12	111.0 (2)	H9A—C9—H9C	109.5
C10—N2—C12	110.3 (2)	H9B—C9—H9C	109.5
C8—N2—H2	106.3	N2—C10—C11	113.8 (3)
C10—N2—H2	106.3	N2—C10—H10A	108.8
C12—N2—H2	106.3	C11—C10—H10A	108.8
C2—C1—C6	122.14 (16)	N2—C10—H10B	108.8
C2—C1—S1	117.11 (13)	C11—C10—H10B	108.8
C6—C1—S1	120.61 (13)	H10A—C10—H10B	107.7
C1—C2—C3	121.14 (16)	C10—C11—H11A	109.5
C1—C2—H2A	119.4	C10—C11—H11B	109.5
C3—C2—H2A	119.4	H11A—C11—H11B	109.5
N1—C3—C2	120.89 (17)	C10—C11—H11C	109.5
N1—C3—C4	121.55 (17)	H11A—C11—H11C	109.5
C2—C3—C4	117.54 (16)	H11B—C11—H11C	109.5
C5—C4—C3	120.61 (17)	C13—C12—N2	112.7 (2)
C5—C4—H4	119.7	C13—C12—H12A	109.1
C3—C4—H4	119.7	N2—C12—H12A	109.1
C4—C5—C6	122.96 (17)	C13—C12—H12B	109.1
C4—C5—H5	118.5	N2—C12—H12B	109.1
C6—C5—H5	118.5	H12A—C12—H12B	107.8
C5—C6—C1	115.55 (16)	C12—C13—H13A	109.5
C5—C6—C7	122.02 (16)	C12—C13—H13B	109.5
C1—C6—C7	122.43 (16)	H13A—C13—H13B	109.5
C7^{i}—C7—C6	125.2 (2)	C12—C13—H13C	109.5
C7^{i}—C7—H7	117.4	H13A—C13—H13C	109.5
C6—C7—H7	117.4	H13B—C13—H13C	109.5

O1—S1—C1—C2	6.48 (18)	C4—C5—C6—C7	−177.47 (18)
O3—S1—C1—C2	−114.99 (15)	C2—C1—C6—C5	−1.6 (3)
O2—S1—C1—C2	126.33 (15)	S1—C1—C6—C5	−177.21 (14)
O1—S1—C1—C6	−177.67 (15)	C2—C1—C6—C7	177.78 (17)
O3—S1—C1—C6	60.86 (17)	S1—C1—C6—C7	2.1 (2)
O2—S1—C1—C6	−57.81 (16)	C5—C6—C7—C7^{i}	15.7 (4)
C6—C1—C2—C3	−0.4 (3)	C1—C6—C7—C7^{i}	−163.6 (2)

S1—C1—C2—C3	175.34 (14)	C10—N2—C8—C9	60.4 (4)
C1—C2—C3—N1	−176.21 (18)	C12—N2—C8—C9	−172.7 (3)
C1—C2—C3—C4	2.2 (3)	C8—N2—C10—C11	58.6 (5)
N1—C3—C4—C5	176.50 (19)	C12—N2—C10—C11	−68.6 (4)
C2—C3—C4—C5	−1.9 (3)	C8—N2—C12—C13	68.8 (3)
C3—C4—C5—C6	−0.2 (3)	C10—N2—C12—C13	−161.4 (2)
C4—C5—C6—C1	1.9 (3)		

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1^{ii}	0.87	2.17	2.946 (2)	149
N1—H1B···O3^{iii}	0.87	2.06	2.915 (2)	166
N2—H2···O2^{iv}	0.92	1.84	2.747 (2)	171

Symmetry codes: (ii) −*x*+1, −*y*+2, −*z*+2; (iii) *x*+1, *y*, *z*; (iv) −*x*, −*y*+2, −*z*+1.

Fig. 1

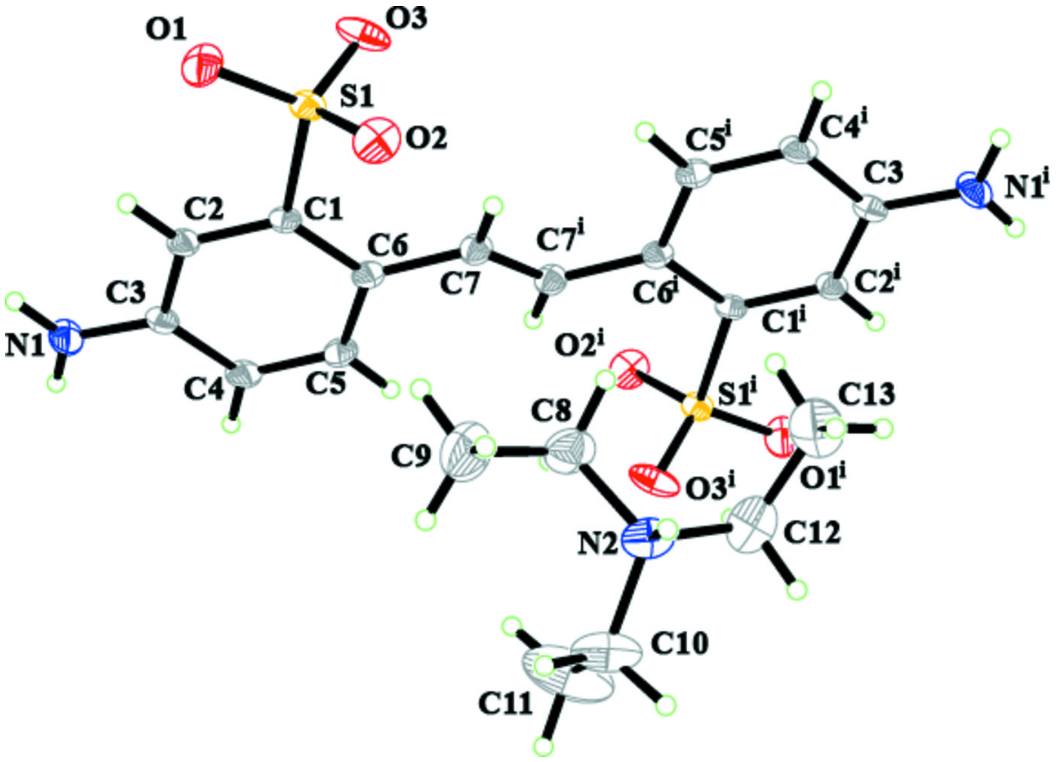

O1
O3
S1
O2
C2
C1
C6
C7
C7i
C6i
C5i
C4i
C3
N1i
C2i
C1i
N1
C3
C4
C5
O2i
C8
S1i
C13
C9
O3i
O1i
N2
C12
C10
C11

Fig. 2

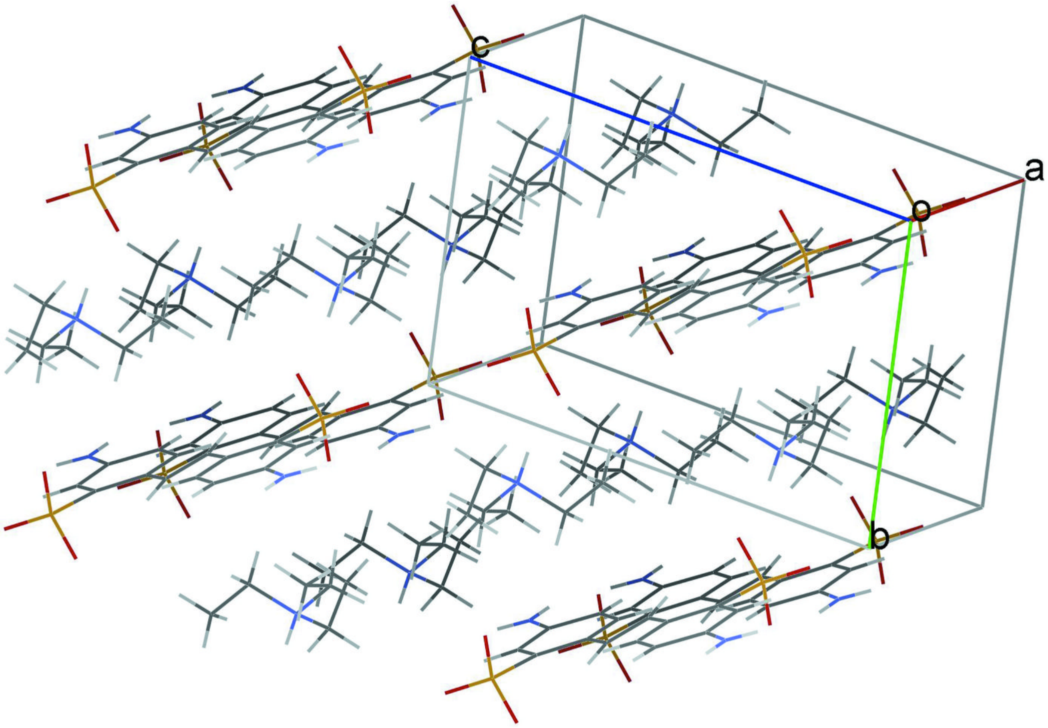


Fig. 3

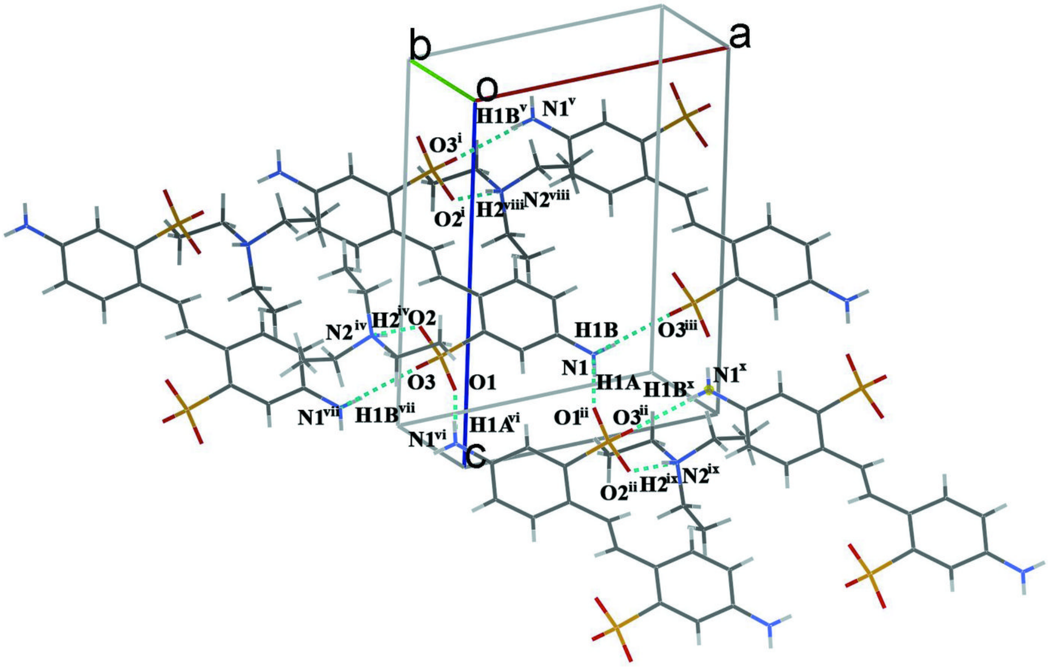
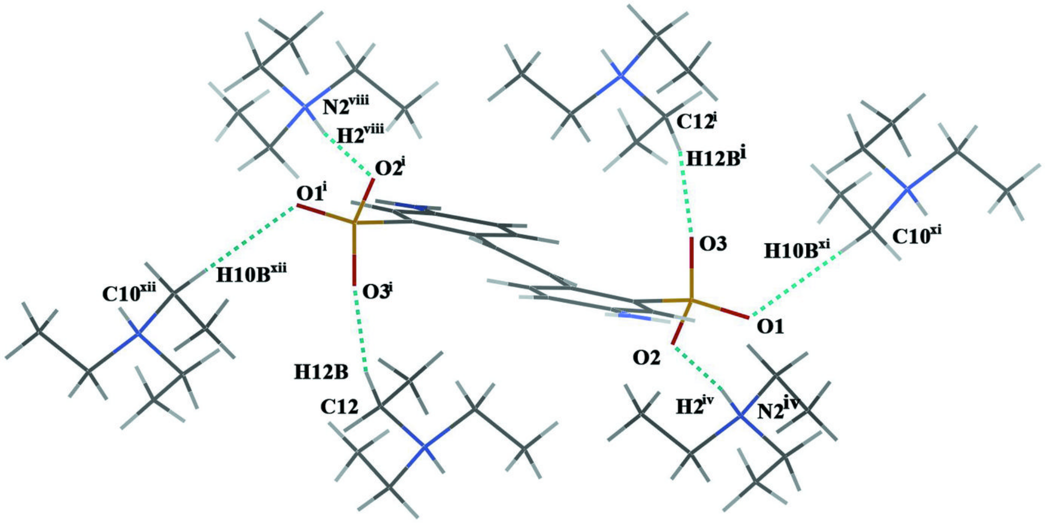

b
o
a
c
$H1B^{v}$
$N1^{v}$
$O3^{i}$
$O2^{i}$
$H2^{viii}$
$N2^{viii}$
$N2^{iv}$
$H2^{iv}$
O2
O3
O1
H1B
$O3^{iii}$
N1
H1A
$H1B^{x}$
$N1^{x}$
$N1^{vii}$
$H1B^{vii}$
$N1^{vi}$
$H1A^{vi}$
$O1^{ii}$
$O3^{ii}$
$O2^{ii}$
$H2^{ix}$
$N2^{ix}$

Fig. 4


N2viii
H2viii
O2i
O1i
H10Bxii
C10xii
O3i
H12B
C12
C12i
H12Bi
O3
H10Bxi
C10xi
O1
O2
H2iv
N2iv