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2-Aminoanilinium benzene-1,2-diaminium tris(4-methylbenzene-1-sulfonate)

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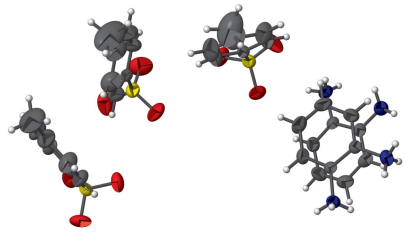
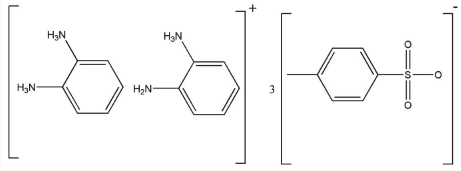
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_{10}N_2^{2+}\cdot C_6H_9N_2^{+}\cdot 3C_7H_7O_3S^{-}$, one of the cations is doubly protonated and one is singly protonated with charge balance achieved by three sulfonate anions. The crystal packing features N—H···O and C—H···O hydrogen bonds. The ions are arranged into a two-dimensional network along the (010) plane and the structure is further consolidated by weak C—H···π interactions.

3D view



Chemical scheme



Structure description

A variety of pharmaceutical drugs are prepared as salts of benzenesulfonic acid. Recently, much attention has been devoted to simple molecular–ionic crystals containing organic cations and anions because of the tunability of their special structural features and their interesting physical properties (Katrusiak & Szafrański, 2006). In a continuation of our studies of molecular compounds with non-linear optical properties that are used in optoelectronic and photonic devices (Nalwa & Miyata, 1997), we herewith report the crystal structure of the title compound (Fig. 1). One of the cations is doubly protonated (at N1 and N2) and the other is singly protonated at N4. The geometric parameters agree well with reported similar structures (Jasinski *et al.*, 2011; Krishnakumar *et al.*, 2012).

The dihedral angles between the C22–C27 benzene ring of one of the cations and the C1–C6, C8–C13 and C15–C20 benzene rings of the anions are 70.63 (16), 75.67 (16) and 86.29 (16)°, respectively. The C28–C33 benzene ring of one of the cations makes dihedral angles of 63.57 (15), 69.42 (15) and 87.04 (16)°, respectively, with the C1–C6, C8–C13 and C15–C20 benzene rings of the anions.

The crystal packing features N—H···O and C—H···O hydrogen bonds (Fig. 2, Table 1). The ions are arranged into a two-dimensional network parallel to the (010) plane and the structure is further consolidated by weak C—H···π interactions (Table 1).

OPEN ACCESS

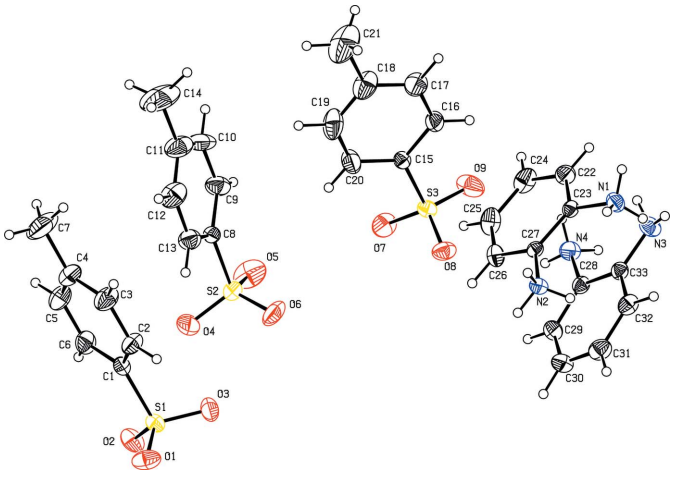


Figure 1
The molecular structure of the title molecular salt, with the atom labelling and 30% probability displacement ellipsoids.

An weak π–π stacking interaction is observed between the C22–C27 and C28–C33 benzene rings of the cations, with a centroid-to-centroid distance of 3.7565 (17) Å.

Synthesis and crystallization

o-Phenylediamine (1.36 g) and *p*-toluenesulfonic acid (2.3 g) were mixed in a 1:2 ratio in water at ambient temperature and the solution was stirred for five hours, then filtered and placed in a beaker covered with perforated polythene. Colourless crystals of the title molecular salt were recovered after one week.

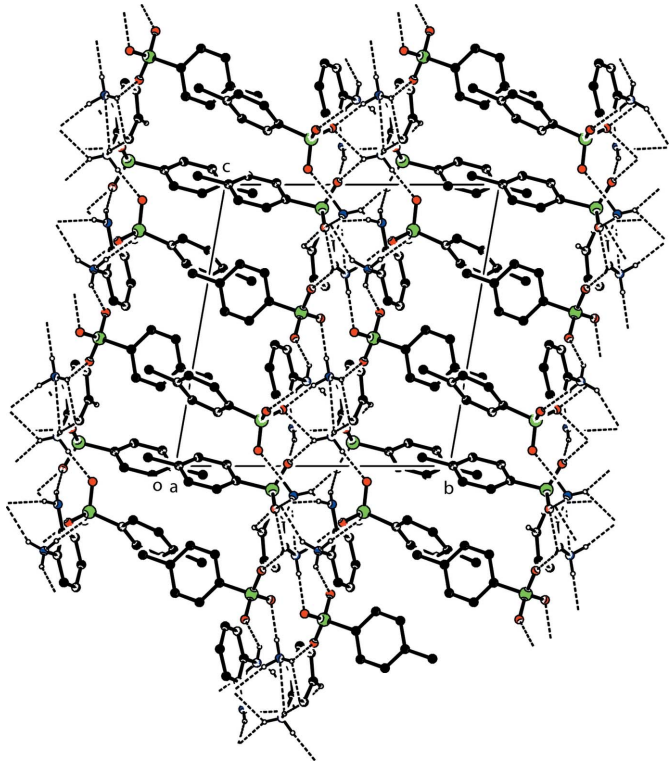


Figure 2
The crystal packing of the title molecular salt viewed along the *a* axis. The hydrogen bonds (Table 1) are shown as dashed lines. H atoms not involving in hydrogen bonding have been omitted for clarity.

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

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C1–C6, C8–C13 and C15–C20 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*A*···O8^{i}	0.87 (1)	1.91 (1)	2.785 (3)	175 (3)
N2—H2*B*···O6^{i}	0.87 (1)	1.86 (1)	2.707 (3)	164 (3)
N3—H3*A*···O3^{i}	0.86 (1)	2.28 (1)	3.113 (3)	164 (3)
N1—H1*A*···O3^{i}	0.86 (1)	2.06 (2)	2.810 (3)	144 (3)
N1—H1*A*···O6^{i}	0.86 (1)	2.44 (3)	2.852 (4)	110 (3)
N3—H3*B*···O1^{ii}	0.86 (1)	2.15 (1)	2.989 (4)	163 (3)
N4—H4*B*···O1^{ii}	0.87 (1)	2.12 (2)	2.910 (4)	150 (3)
C24—H24···O1^{ii}	0.93	2.55	3.197 (4)	127
N1—H1*C*···O4^{iii}	0.87 (1)	1.84 (1)	2.698 (3)	169 (4)
N1—H1*B*···O2^{iii}	0.86 (1)	1.83 (1)	2.669 (3)	164 (3)
N2—H2*C*···O2^{iii}	0.87 (1)	2.30 (3)	2.873 (3)	124 (2)
N2—H2*C*···O9^{iv}	0.87 (1)	2.07 (2)	2.833 (3)	146 (3)
N4—H4*A*···O5^{v}	0.87 (1)	1.88 (1)	2.742 (4)	175 (4)
N4—H4*C*···O7^{v}	0.87 (1)	2.06 (2)	2.826 (3)	147 (4)
C5—H5···*Cg*2^{vi}	0.93	2.87	3.629 (4)	140
C10—H10···*Cg*3^{vii}	0.93	2.81	3.587 (5)	142
C13—H13···*Cg*1	0.93	2.93	3.609 (3)	131

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_{10}N_2^{2+}\cdot C_6H_9N_2^{+}\cdot 3C_7H_7O_3S^{-}$
M_r	732.87
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, *b*, *c* (Å)	10.5058 (4), 12.8929 (4), 14.0425 (4)
α, β, γ (°)	80.187 (2), 73.218 (1), 89.188 (2)
V (Å^3)	1793.17 (10)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.24 × 0.20 × 0.18
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32987, 6325, 4091
R_{int}	0.059
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.117, 1.03
No. of reflections	6325
No. of parameters	489
No. of restraints	11
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.36

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXT2016* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2018). **3**, x180437 [https://doi.org/10.1107/S2414314618004376]

2-Aminoanilinium benzene-1,2-diaminium tris(4-methylbenzene-1-sulfonate)

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2-Aminoanilinium benzene-1,2-diaminium tris(4-methylbenzene-1-sulfonate)

Crystal data

$C_6H_{10}N_2^{2+}\cdot C_6H_9N_2^{+}\cdot 3C_7H_7O_3S^{-}$
M_r = 732.87
Triclinic, $P\overline{1}$
a = 10.5058 (4) Å
b = 12.8929 (4) Å
c = 14.0425 (4) Å
α = 80.187 (2)°
β = 73.218 (1)°
γ = 89.188 (2)°
V = 1793.17 (10) Å^3
Z = 2
$F(000)$ = 772
D_x = 1.357 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7569 reflections
θ = 2.4–26.2°
μ = 0.26 mm^{-1}
T = 295 K
Block, colourless
0.24 × 0.20 × 0.18 mm

Data collection

Bruker APEXII CCD diffractometer
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2004)
32987 measured reflections
6325 independent reflections
4091 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 25.0°, θ_{min} = 2.0°
h = −12→12
k = −15→15
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.03
6325 reflections
489 parameters
11 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.6864P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. C-bound H atoms were placed in calculated positions and allowed to ride on their carrier atoms, with C—H = 0.93 Å (aromatic CH) or 0.96 Å (methyl CH), and with $U_{iso} = 1.5U_{eq}$(methyl C) or $U_{iso} = 1.2U_{eq}$(aromatic C). H atoms for NH groups were located in difference-Fourier maps and refined with a distance restraint of N—H = 0.86 (1) Å.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7325 (3)	0.7693 (2)	0.05175 (19)	0.0359 (7)
C2	0.8554 (3)	0.8136 (2)	−0.0052 (2)	0.0500 (8)
H2	0.926511	0.770800	−0.026143	0.060*
C3	0.8723 (4)	0.9218 (3)	−0.0310 (3)	0.0648 (10)
H3	0.955466	0.950946	−0.069595	0.078*
C4	0.7699 (4)	0.9875 (3)	−0.0014 (3)	0.0671 (10)
C5	0.6483 (4)	0.9424 (3)	0.0555 (3)	0.0705 (11)
H5	0.577680	0.985428	0.076773	0.085*
C6	0.6285 (3)	0.8346 (3)	0.0817 (2)	0.0540 (8)
H6	0.544987	0.805795	0.119751	0.065*
C7	0.7897 (5)	1.1056 (3)	−0.0308 (4)	0.1138 (17)
H7A	0.809013	1.133881	0.022713	0.171*
H7B	0.710080	1.135453	−0.042370	0.171*
H7C	0.862444	1.122681	−0.091320	0.171*
C8	0.5243 (3)	0.8441 (2)	−0.21536 (19)	0.0378 (7)
C9	0.4702 (3)	0.9086 (3)	−0.2808 (2)	0.0589 (9)
H9	0.397778	0.885012	−0.297780	0.071*
C10	0.5252 (4)	1.0099 (3)	−0.3215 (3)	0.0785 (12)
H10	0.488594	1.053475	−0.365877	0.094*
C11	0.6309 (4)	1.0465 (3)	−0.2980 (3)	0.0758 (11)
C12	0.6838 (4)	0.9814 (3)	−0.2342 (3)	0.0705 (10)
H12	0.756892	1.005325	−0.218288	0.085*
C13	0.6323 (3)	0.8803 (3)	−0.1919 (2)	0.0543 (8)
H13	0.670179	0.837317	−0.147991	0.065*
C14	0.6870 (5)	1.1583 (3)	−0.3426 (4)	0.141 (2)
H14A	0.770246	1.167096	−0.328980	0.211*
H14B	0.625384	1.207543	−0.312706	0.211*
H14C	0.700713	1.170618	−0.414314	0.211*
C15	0.6807 (3)	0.7641 (2)	−0.58539 (19)	0.0333 (6)
C16	0.7424 (3)	0.7992 (2)	−0.6864 (2)	0.0470 (8)
H16	0.736544	0.758539	−0.733751	0.056*
C17	0.8127 (3)	0.8942 (3)	−0.7177 (3)	0.0659 (10)
H17	0.853231	0.917137	−0.786234	0.079*
C18	0.8242 (4)	0.9555 (3)	−0.6501 (3)	0.0733 (11)
C19	0.7625 (4)	0.9197 (3)	−0.5492 (3)	0.0772 (12)
H19	0.769364	0.960268	−0.502023	0.093*
C20	0.6906 (3)	0.8247 (3)	−0.5163 (2)	0.0587 (9)
H20	0.649245	0.802078	−0.447786	0.070*
C21	0.8996 (5)	1.0613 (3)	−0.6843 (4)	0.131 (2)
H21A	0.993507	1.050309	−0.704886	0.196*
H21B	0.878881	1.100075	−0.629430	0.196*
H21C	0.874198	1.100383	−0.740054	0.196*
C22	1.2542 (3)	0.5750 (2)	−0.81322 (19)	0.0314 (6)
C23	1.1471 (3)	0.6203 (2)	−0.8383 (2)	0.0463 (8)
H23	1.148923	0.637179	−0.905753	0.056*

C24	1.0372 (3)	0.6410 (3)	−0.7643 (3)	0.0568 (9)
H24	0.965305	0.673123	−0.781748	0.068*
C25	1.0328 (3)	0.6145 (3)	−0.6645 (3)	0.0557 (9)
H25	0.957297	0.626978	−0.614244	0.067*
C26	1.1407 (3)	0.5694 (2)	−0.6391 (2)	0.0435 (7)
H26	1.137998	0.551588	−0.571492	0.052*
C27	1.2523 (2)	0.55048 (19)	−0.71291 (18)	0.0291 (6)
C28	0.8648 (3)	0.3735 (2)	−0.68323 (19)	0.0342 (6)
C29	0.8651 (3)	0.3320 (2)	−0.5866 (2)	0.0448 (7)
H29	0.789832	0.335811	−0.532796	0.054*
C30	0.9761 (3)	0.2849 (2)	−0.5691 (2)	0.0530 (8)
H30	0.976860	0.256931	−0.503717	0.064*
C31	1.0864 (3)	0.2798 (2)	−0.6499 (3)	0.0525 (8)
H31	1.162248	0.248455	−0.638725	0.063*
C32	1.0857 (3)	0.3202 (2)	−0.7462 (2)	0.0441 (7)
H32	1.161153	0.315704	−0.799655	0.053*
C33	0.9741 (3)	0.3680 (2)	−0.76597 (19)	0.0354 (7)
N1	1.3660 (3)	0.5504 (2)	−0.89483 (19)	0.0429 (6)
N2	1.3655 (2)	0.5040 (2)	−0.68291 (18)	0.0352 (6)
N3	0.9729 (3)	0.4043 (2)	−0.86411 (19)	0.0491 (7)
N4	0.7447 (3)	0.4232 (2)	−0.6989 (2)	0.0455 (6)
O1	0.8136 (2)	0.59810 (16)	0.13209 (17)	0.0612 (6)
O2	0.57959 (19)	0.60896 (17)	0.15234 (14)	0.0560 (6)
O3	0.7300 (2)	0.59162 (16)	−0.00861 (14)	0.0557 (6)
O4	0.4293 (3)	0.70824 (18)	−0.05549 (16)	0.0840 (8)
O5	0.3438 (3)	0.7040 (2)	−0.1939 (2)	0.0908 (9)
O6	0.5632 (2)	0.64617 (17)	−0.20037 (18)	0.0720 (7)
O7	0.4923 (2)	0.64765 (17)	−0.45485 (16)	0.0636 (6)
O8	0.6954 (2)	0.56619 (16)	−0.52454 (15)	0.0532 (6)
O9	0.5535 (3)	0.61892 (18)	−0.62836 (16)	0.0757 (8)
S1	0.71235 (7)	0.63186 (6)	0.08397 (5)	0.0366 (2)
S2	0.45907 (8)	0.71568 (6)	−0.16259 (6)	0.0451 (2)
S3	0.59663 (7)	0.64019 (6)	−0.54542 (5)	0.0387 (2)
H1A	1.355 (4)	0.4892 (14)	−0.909 (3)	0.088 (13)*
H1B	1.4393 (18)	0.557 (3)	−0.880 (2)	0.064 (11)*
H1C	1.377 (4)	0.599 (2)	−0.9477 (17)	0.089 (14)*
H2A	1.342 (3)	0.4814 (19)	−0.6177 (8)	0.043 (8)*
H2B	1.398 (3)	0.4519 (18)	−0.713 (2)	0.074 (12)*
H2C	1.430 (2)	0.5497 (19)	−0.693 (2)	0.062 (10)*
H3A	1.0508 (15)	0.417 (2)	−0.9065 (16)	0.048 (9)*
H3B	0.921 (3)	0.4550 (17)	−0.875 (2)	0.058 (11)*
H4A	0.714 (4)	0.386 (3)	−0.734 (3)	0.098 (15)*
H4B	0.757 (3)	0.4879 (12)	−0.731 (2)	0.073 (12)*
H4C	0.683 (3)	0.423 (3)	−0.6426 (16)	0.101 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0353 (17)	0.0430 (17)	0.0305 (14)	0.0038 (14)	−0.0100 (13)	−0.0083 (13)
C2	0.044 (2)	0.0362 (19)	0.062 (2)	0.0026 (15)	−0.0023 (16)	−0.0098 (15)
C3	0.061 (2)	0.043 (2)	0.076 (2)	−0.0075 (18)	0.0018 (19)	−0.0074 (18)
C4	0.088 (3)	0.040 (2)	0.071 (2)	0.014 (2)	−0.018 (2)	−0.0114 (18)
C5	0.074 (3)	0.058 (3)	0.080 (3)	0.034 (2)	−0.017 (2)	−0.024 (2)
C6	0.045 (2)	0.061 (2)	0.0524 (19)	0.0132 (17)	−0.0056 (16)	−0.0168 (17)
C7	0.143 (4)	0.040 (2)	0.151 (4)	0.014 (3)	−0.034 (4)	−0.014 (3)
C8	0.0439 (18)	0.0353 (17)	0.0313 (15)	0.0106 (14)	−0.0072 (13)	−0.0049 (13)
C9	0.056 (2)	0.061 (2)	0.057 (2)	0.0124 (18)	−0.0212 (18)	0.0031 (18)
C10	0.087 (3)	0.062 (3)	0.066 (2)	0.022 (2)	−0.011 (2)	0.023 (2)
C11	0.069 (3)	0.052 (2)	0.078 (3)	0.003 (2)	0.010 (2)	0.010 (2)
C12	0.058 (2)	0.055 (2)	0.091 (3)	−0.0095 (19)	−0.011 (2)	−0.011 (2)
C13	0.057 (2)	0.049 (2)	0.057 (2)	0.0071 (17)	−0.0188 (17)	−0.0054 (16)
C14	0.135 (5)	0.059 (3)	0.165 (5)	−0.015 (3)	0.025 (4)	0.035 (3)
C15	0.0302 (16)	0.0368 (16)	0.0320 (15)	0.0018 (12)	−0.0075 (12)	−0.0062 (12)
C16	0.053 (2)	0.0442 (19)	0.0387 (17)	−0.0027 (15)	−0.0038 (15)	−0.0094 (14)
C17	0.069 (3)	0.052 (2)	0.056 (2)	−0.0121 (19)	0.0116 (18)	−0.0040 (18)
C18	0.059 (2)	0.054 (2)	0.095 (3)	−0.0189 (19)	0.001 (2)	−0.021 (2)
C19	0.081 (3)	0.076 (3)	0.084 (3)	−0.013 (2)	−0.022 (2)	−0.044 (2)
C20	0.070 (2)	0.064 (2)	0.0426 (18)	−0.0095 (19)	−0.0111 (17)	−0.0163 (17)
C21	0.117 (4)	0.078 (3)	0.168 (5)	−0.051 (3)	0.018 (4)	−0.040 (3)
C22	0.0325 (16)	0.0277 (15)	0.0343 (15)	−0.0010 (12)	−0.0093 (13)	−0.0069 (12)
C23	0.052 (2)	0.0447 (19)	0.0503 (18)	0.0061 (16)	−0.0275 (17)	−0.0096 (15)
C24	0.043 (2)	0.058 (2)	0.085 (3)	0.0179 (16)	−0.0356 (19)	−0.0264 (19)
C25	0.0298 (18)	0.071 (2)	0.069 (2)	0.0075 (16)	−0.0082 (16)	−0.0322 (19)
C26	0.0377 (18)	0.053 (2)	0.0394 (16)	0.0000 (15)	−0.0062 (14)	−0.0168 (14)
C27	0.0286 (15)	0.0252 (14)	0.0345 (15)	−0.0006 (12)	−0.0104 (12)	−0.0052 (11)
C28	0.0317 (16)	0.0318 (16)	0.0373 (16)	0.0033 (12)	−0.0066 (13)	−0.0070 (13)
C29	0.047 (2)	0.0477 (19)	0.0355 (16)	0.0009 (15)	−0.0055 (14)	−0.0062 (14)
C30	0.067 (2)	0.051 (2)	0.0431 (18)	0.0044 (17)	−0.0228 (18)	−0.0009 (15)
C31	0.049 (2)	0.049 (2)	0.066 (2)	0.0089 (16)	−0.0274 (18)	−0.0090 (17)
C32	0.0329 (17)	0.0420 (18)	0.0548 (19)	0.0045 (14)	−0.0079 (15)	−0.0100 (15)
C33	0.0364 (17)	0.0329 (16)	0.0350 (16)	−0.0003 (13)	−0.0069 (13)	−0.0067 (13)
N1	0.0475 (18)	0.0478 (18)	0.0314 (14)	−0.0006 (14)	−0.0081 (13)	−0.0071 (13)
N2	0.0354 (15)	0.0369 (16)	0.0321 (14)	0.0021 (12)	−0.0107 (12)	−0.0009 (12)
N3	0.0421 (18)	0.062 (2)	0.0355 (15)	0.0089 (15)	−0.0029 (14)	−0.0019 (14)
N4	0.0370 (17)	0.0503 (19)	0.0405 (16)	0.0109 (14)	−0.0014 (14)	−0.0025 (15)
O1	0.0547 (14)	0.0508 (14)	0.0867 (16)	−0.0012 (11)	−0.0447 (13)	0.0072 (12)
O2	0.0408 (13)	0.0758 (16)	0.0386 (11)	−0.0182 (11)	0.0041 (10)	−0.0007 (11)
O3	0.0690 (15)	0.0557 (14)	0.0384 (11)	−0.0137 (11)	−0.0041 (11)	−0.0157 (10)
O4	0.140 (2)	0.0519 (15)	0.0405 (13)	−0.0117 (15)	−0.0027 (14)	0.0045 (11)
O5	0.0742 (18)	0.0717 (18)	0.139 (2)	−0.0116 (14)	−0.0529 (18)	−0.0133 (17)
O6	0.0810 (18)	0.0399 (13)	0.0926 (18)	0.0209 (12)	−0.0150 (14)	−0.0237 (12)
O7	0.0456 (14)	0.0586 (15)	0.0630 (14)	−0.0003 (11)	0.0181 (11)	−0.0047 (11)
O8	0.0467 (13)	0.0462 (13)	0.0560 (13)	0.0120 (10)	−0.0059 (11)	0.0041 (10)

O9	0.107 (2)	0.0680 (16)	0.0621 (15)	−0.0359 (14)	−0.0489 (14)	0.0073 (12)
S1	0.0338 (4)	0.0428 (4)	0.0319 (4)	−0.0060 (3)	−0.0097 (3)	−0.0026 (3)
S2	0.0539 (5)	0.0359 (4)	0.0453 (5)	0.0034 (4)	−0.0132 (4)	−0.0083 (3)
S3	0.0387 (4)	0.0400 (4)	0.0334 (4)	−0.0016 (3)	−0.0077 (3)	−0.0003 (3)

Geometric parameters (Å, º)

C1—C2	1.379 (4)	C22—C23	1.368 (4)
C1—C6	1.381 (4)	C22—C27	1.385 (3)
C1—S1	1.753 (3)	C22—N1	1.459 (4)
C2—C3	1.381 (4)	C23—C24	1.370 (4)
C2—H2	0.9300	C23—H23	0.9300
C3—C4	1.373 (5)	C24—C25	1.372 (4)
C3—H3	0.9300	C24—H24	0.9300
C4—C5	1.372 (5)	C25—C26	1.377 (4)
C4—C7	1.509 (5)	C25—H25	0.9300
C5—C6	1.378 (5)	C26—C27	1.373 (4)
C5—H5	0.9300	C26—H26	0.9300
C6—H6	0.9300	C27—N2	1.460 (3)
C7—H7A	0.9600	C28—C29	1.372 (4)
C7—H7B	0.9600	C28—C33	1.389 (4)
C7—H7C	0.9600	C28—N4	1.463 (4)
C8—C9	1.374 (4)	C29—C30	1.372 (4)
C8—C13	1.378 (4)	C29—H29	0.9300
C8—S2	1.755 (3)	C30—C31	1.378 (4)
C9—C10	1.393 (5)	C30—H30	0.9300
C9—H9	0.9300	C31—C32	1.366 (4)
C10—C11	1.358 (5)	C31—H31	0.9300
C10—H10	0.9300	C32—C33	1.392 (4)
C11—C12	1.354 (5)	C32—H32	0.9300
C11—C14	1.523 (5)	C33—N3	1.382 (4)
C12—C13	1.383 (4)	N1—H1A	0.863 (10)
C12—H12	0.9300	N1—H1B	0.864 (10)
C13—H13	0.9300	N1—H1C	0.867 (10)
C14—H14A	0.9600	N2—H2A	0.874 (10)
C14—H14B	0.9600	N2—H2B	0.869 (10)
C14—H14C	0.9600	N2—H2C	0.868 (10)
C15—C20	1.372 (4)	N3—H3A	0.860 (10)
C15—C16	1.377 (4)	N3—H3B	0.862 (10)
C15—S3	1.759 (3)	N4—H4A	0.867 (10)
C16—C17	1.376 (4)	N4—H4B	0.868 (10)
C16—H16	0.9300	N4—H4C	0.865 (10)
C17—C18	1.365 (5)	O1—S1	1.442 (2)
C17—H17	0.9300	O2—S1	1.4478 (19)
C18—C19	1.378 (5)	O3—S1	1.4428 (19)
C18—C21	1.518 (5)	O4—S2	1.431 (2)
C19—C20	1.385 (5)	O5—S2	1.421 (2)
C19—H19	0.9300	O6—S2	1.442 (2)

C20—H20	0.9300	O7—S3	1.436 (2)
C21—H21A	0.9600	O8—S3	1.458 (2)
C21—H21B	0.9600	O9—S3	1.433 (2)
C21—H21C	0.9600		

C2—C1—C6	119.0 (3)	C27—C22—N1	122.1 (2)
C2—C1—S1	119.1 (2)	C22—C23—C24	120.2 (3)
C6—C1—S1	121.8 (2)	C22—C23—H23	119.9
C1—C2—C3	119.6 (3)	C24—C23—H23	119.9
C1—C2—H2	120.2	C23—C24—C25	120.2 (3)
C3—C2—H2	120.2	C23—C24—H24	119.9
C4—C3—C2	121.9 (3)	C25—C24—H24	119.9
C4—C3—H3	119.0	C24—C25—C26	119.7 (3)
C2—C3—H3	119.0	C24—C25—H25	120.1
C5—C4—C3	117.8 (3)	C26—C25—H25	120.1
C5—C4—C7	120.9 (4)	C27—C26—C25	120.4 (3)
C3—C4—C7	121.3 (4)	C27—C26—H26	119.8
C4—C5—C6	121.4 (3)	C25—C26—H26	119.8
C4—C5—H5	119.3	C26—C27—C22	119.3 (3)
C6—C5—H5	119.3	C26—C27—N2	118.7 (2)
C5—C6—C1	120.2 (3)	C22—C27—N2	121.9 (2)
C5—C6—H6	119.9	C29—C28—C33	121.8 (3)
C1—C6—H6	119.9	C29—C28—N4	118.6 (3)
C4—C7—H7A	109.5	C33—C28—N4	119.5 (2)
C4—C7—H7B	109.5	C28—C29—C30	120.2 (3)
H7A—C7—H7B	109.5	C28—C29—H29	119.9
C4—C7—H7C	109.5	C30—C29—H29	119.9
H7A—C7—H7C	109.5	C29—C30—C31	119.0 (3)
H7B—C7—H7C	109.5	C29—C30—H30	120.5
C9—C8—C13	119.4 (3)	C31—C30—H30	120.5
C9—C8—S2	121.0 (2)	C32—C31—C30	120.8 (3)
C13—C8—S2	119.6 (2)	C32—C31—H31	119.6
C8—C9—C10	119.3 (3)	C30—C31—H31	119.6
C8—C9—H9	120.4	C31—C32—C33	121.3 (3)
C10—C9—H9	120.4	C31—C32—H32	119.4
C11—C10—C9	121.6 (3)	C33—C32—H32	119.4
C11—C10—H10	119.2	N3—C33—C28	122.5 (3)
C9—C10—H10	119.2	N3—C33—C32	120.6 (3)
C12—C11—C10	118.3 (3)	C28—C33—C32	116.9 (3)
C12—C11—C14	121.5 (4)	C22—N1—H1A	111 (2)
C10—C11—C14	120.2 (4)	C22—N1—H1B	110 (2)
C11—C12—C13	122.0 (4)	H1A—N1—H1B	113 (3)
C11—C12—H12	119.0	C22—N1—H1C	109 (2)
C13—C12—H12	119.0	H1A—N1—H1C	111 (3)
C8—C13—C12	119.4 (3)	H1B—N1—H1C	102 (3)
C8—C13—H13	120.3	C27—N2—H2A	109.6 (18)
C12—C13—H13	120.3	C27—N2—H2B	113 (2)
C11—C14—H14A	109.5	H2A—N2—H2B	108 (3)

C11—C14—H14B	109.5	C27—N2—H2C	113 (2)
H14A—C14—H14B	109.5	H2A—N2—H2C	104 (3)
C11—C14—H14C	109.5	H2B—N2—H2C	108 (3)
H14A—C14—H14C	109.5	C33—N3—H3A	114.0 (19)
H14B—C14—H14C	109.5	C33—N3—H3B	118 (2)
C20—C15—C16	119.2 (3)	H3A—N3—H3B	110 (3)
C20—C15—S3	120.6 (2)	C28—N4—H4A	107 (3)
C16—C15—S3	120.1 (2)	C28—N4—H4B	115 (2)
C17—C16—C15	120.4 (3)	H4A—N4—H4B	108 (3)
C17—C16—H16	119.8	C28—N4—H4C	112 (3)
C15—C16—H16	119.8	H4A—N4—H4C	107 (4)
C18—C17—C16	121.3 (3)	H4B—N4—H4C	107 (3)
C18—C17—H17	119.3	O1—S1—O3	112.34 (14)
C16—C17—H17	119.3	O1—S1—O2	112.08 (13)
C17—C18—C19	117.9 (3)	O3—S1—O2	112.18 (12)
C17—C18—C21	121.6 (4)	O1—S1—C1	105.76 (12)
C19—C18—C21	120.5 (4)	O3—S1—C1	107.14 (12)
C18—C19—C20	121.6 (3)	O2—S1—C1	106.84 (13)
C18—C19—H19	119.2	O5—S2—O4	112.67 (18)
C20—C19—H19	119.2	O5—S2—O6	113.46 (16)
C15—C20—C19	119.5 (3)	O4—S2—O6	111.30 (16)
C15—C20—H20	120.3	O5—S2—C8	106.66 (15)
C19—C20—H20	120.3	O4—S2—C8	106.07 (13)
C18—C21—H21A	109.5	O6—S2—C8	106.05 (14)
C18—C21—H21B	109.5	O9—S3—O7	115.46 (15)
H21A—C21—H21B	109.5	O9—S3—O8	111.31 (14)
C18—C21—H21C	109.5	O7—S3—O8	111.09 (13)
H21A—C21—H21C	109.5	O9—S3—C15	106.42 (12)
H21B—C21—H21C	109.5	O7—S3—C15	106.38 (12)
C23—C22—C27	120.1 (3)	O8—S3—C15	105.44 (12)
C23—C22—N1	117.8 (2)		

C6—C1—C2—C3	0.1 (4)	C25—C26—C27—C22	−1.5 (4)
S1—C1—C2—C3	180.0 (2)	C25—C26—C27—N2	179.0 (3)
C1—C2—C3—C4	0.1 (5)	C23—C22—C27—C26	1.9 (4)
C2—C3—C4—C5	0.0 (5)	N1—C22—C27—C26	−175.8 (2)
C2—C3—C4—C7	−179.6 (4)	C23—C22—C27—N2	−178.7 (2)
C3—C4—C5—C6	−0.4 (5)	N1—C22—C27—N2	3.6 (4)
C7—C4—C5—C6	179.2 (4)	C33—C28—C29—C30	1.1 (4)
C4—C5—C6—C1	0.7 (5)	N4—C28—C29—C30	−179.9 (3)
C2—C1—C6—C5	−0.5 (4)	C28—C29—C30—C31	−0.2 (4)
S1—C1—C6—C5	179.6 (2)	C29—C30—C31—C32	−0.4 (5)
C13—C8—C9—C10	−0.5 (5)	C30—C31—C32—C33	0.2 (5)
S2—C8—C9—C10	−179.7 (3)	C29—C28—C33—N3	176.5 (3)
C8—C9—C10—C11	−0.1 (6)	N4—C28—C33—N3	−2.6 (4)
C9—C10—C11—C12	0.7 (6)	C29—C28—C33—C32	−1.3 (4)
C9—C10—C11—C14	−179.0 (4)	N4—C28—C33—C32	179.7 (2)
C10—C11—C12—C13	−0.8 (6)	C31—C32—C33—N3	−177.1 (3)

C14—C11—C12—C13	178.9 (4)	C31—C32—C33—C28	0.7 (4)
C9—C8—C13—C12	0.4 (4)	C2—C1—S1—O1	54.1 (2)
S2—C8—C13—C12	179.6 (2)	C6—C1—S1—O1	−126.0 (2)
C11—C12—C13—C8	0.3 (5)	C2—C1—S1—O3	−65.9 (2)
C20—C15—C16—C17	−0.2 (5)	C6—C1—S1—O3	114.0 (2)
S3—C15—C16—C17	−177.4 (3)	C2—C1—S1—O2	173.7 (2)
C15—C16—C17—C18	0.5 (5)	C6—C1—S1—O2	−6.4 (3)
C16—C17—C18—C19	−0.3 (6)	C9—C8—S2—O5	−5.2 (3)
C16—C17—C18—C21	−178.9 (4)	C13—C8—S2—O5	175.6 (2)
C17—C18—C19—C20	−0.1 (6)	C9—C8—S2—O4	−125.6 (3)
C21—C18—C19—C20	178.5 (4)	C13—C8—S2—O4	55.2 (3)
C16—C15—C20—C19	−0.2 (5)	C9—C8—S2—O6	116.0 (3)
S3—C15—C20—C19	177.0 (3)	C13—C8—S2—O6	−63.2 (3)
C18—C19—C20—C15	0.4 (6)	C20—C15—S3—O9	155.4 (3)
C27—C22—C23—C24	−0.5 (4)	C16—C15—S3—O9	−27.4 (3)
N1—C22—C23—C24	177.3 (3)	C20—C15—S3—O7	31.8 (3)
C22—C23—C24—C25	−1.3 (5)	C16—C15—S3—O7	−151.0 (2)
C23—C24—C25—C26	1.6 (5)	C20—C15—S3—O8	−86.3 (3)
C24—C25—C26—C27	−0.2 (5)	C16—C15—S3—O8	90.9 (2)

Hydrogen-bond geometry (Å, º)

Cg1, Cg2 and Cg3 are the centroids of the C1–C6, C8–C13 and C15–C20 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O8^{i}	0.87 (1)	1.91 (1)	2.785 (3)	175 (3)
N2—H2*B*···O6^{i}	0.87 (1)	1.86 (1)	2.707 (3)	164 (3)
N3—H3*A*···O3^{i}	0.86 (1)	2.28 (1)	3.113 (3)	164 (3)
N1—H1*A*···O3^{i}	0.86 (1)	2.06 (2)	2.810 (3)	144 (3)
N1—H1*A*···O6^{i}	0.86 (1)	2.44 (3)	2.852 (4)	110 (3)
N3—H3*B*···O1^{ii}	0.86 (1)	2.15 (1)	2.989 (4)	163 (3)
N4—H4*B*···O1^{ii}	0.87 (1)	2.12 (2)	2.910 (4)	150 (3)
C24—H24···O1^{ii}	0.93	2.55	3.197 (4)	127
N1—H1*C*···O4^{iii}	0.87 (1)	1.84 (1)	2.698 (3)	169 (4)
N1—H1*B*···O2^{iii}	0.86 (1)	1.83 (1)	2.669 (3)	164 (3)
N2—H2*C*···O2^{iii}	0.87 (1)	2.30 (3)	2.873 (3)	124 (2)
N2—H2*C*···O9^{iv}	0.87 (1)	2.07 (2)	2.833 (3)	146 (3)
N4—H4*A*···O5^{v}	0.87 (1)	1.88 (1)	2.742 (4)	175 (4)
N4—H4*C*···O7^{v}	0.87 (1)	2.06 (2)	2.826 (3)	147 (4)
C5—H5···*Cg*2^{vi}	0.93	2.87	3.629 (4)	140
C10—H10···*Cg*3^{vii}	0.93	2.81	3.587 (5)	142
C13—H13···*Cg*1	0.93	2.93	3.609 (3)	131

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