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Piperazine-1,4-dium naphthalene-1,5-disulfonate

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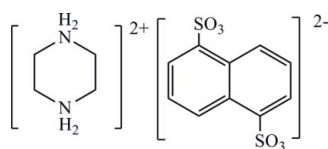
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 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.088; data-to-parameter ratio = 16.8.

The title molecular salt, $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-}$, consists of a piperazinium cation and a 1,5-naphthalenedisulfonate anion. Crystallographic inversion centers are situated at the center of the ring of the dication as well as at the midpoint of the central carbon-carbon bond in the dianion. In the crystal, intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds link the cations and anions.

Related literature

The title compound was obtained during attempts to obtain dielectric-ferroelectric compounds. For general background to ferroelectric metal-organic frameworks, see: Wu *et al.* (2011); Ye *et al.* (2006); Zhang *et al.* (2008, 2010); Fu *et al.* (2009).



Experimental

Crystal data

$\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_{10}\text{H}_6\text{O}_6\text{S}_2^{2-}$
 $M_r = 374.42$
 Monoclinic, $P2_1/c$

$a = 11.997$ (2) Å
 $b = 7.2959$ (15) Å
 $c = 9.1453$ (18) Å

$\beta = 96.00$ (3)°
 $V = 796.1$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.37$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.20 \times 0.20$ mm

Data collection

Rigaku SCXmini diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.955$, $T_{\max} = 0.955$

7956 measured reflections
 1827 independent reflections
 1629 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.088$
 $S = 1.11$
 1827 reflections

109 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1A} \cdots \text{O2}^{\text{i}}$	0.90	1.91	2.7357 (19)	153
$\text{N1}-\text{H1B} \cdots \text{O3}^{\text{ii}}$	0.90	1.91	2.7670 (19)	159

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The author is grateful to the starter fund of Southeast University for the purchase of the diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VM2121).

References

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supporting information

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Piperazine-1,4-dium naphthalene-1,5-disulfonate**Bin Wei****S1. Comment**

Dielectric-ferroelectrics are an interesting class of materials, comprising organic ligands, metal-organic coordination compounds and organic-inorganic hybrids (Fu *et al.*, 2009; Zhang *et al.*, 2010; Zhang *et al.*, 2008; Ye *et al.*, 2006). Unfortunately, the dielectric constant of the title compound as a function of temperature indicates that the permittivity is basically temperature-independent. Below the melting point (402-403K) of the compound, we have found that the title compound has no dielectric disuniformity from 80 K to 405 K. Here we describe the crystal structure of this compound.

The asymmetric unit of the title compound consists of a half piperazinium cation and a half 1,5-naphthalenedisulfonate anion (Fig. 1). The complete molecular structures are generated by inversion centers at the center of the piperazinium ring and at the midpoint of the central carbon-carbon bond in the naphthalene ring. The best planes through the piperazinium ring and the naphthalene ring make a dihedral angle of 80.96 (8)°. The cations and anions are connected by intermolecular N—H···O hydrogen bonds, which contribute to the stability of the crystal structure (Fig. 2 and Table 1).

S2. Experimental

The title compound was obtained by the addition of 1,5-naphthalenedisulfonate acid (3.62 g, 0.01 mol) to a solution of piperazine (0.88 g, 0.01 mol) in water, in the stoichiometric ratio 1: 1. Good quality single crystals were obtained by slow evaporation after two days (yield: 48%).

S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H = 0.93 Å-0.97 Å, N—H = 0.90 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C}, \text{O})$ or $1.5 U_{\text{iso}}(\text{C})$ for methyl H atoms.

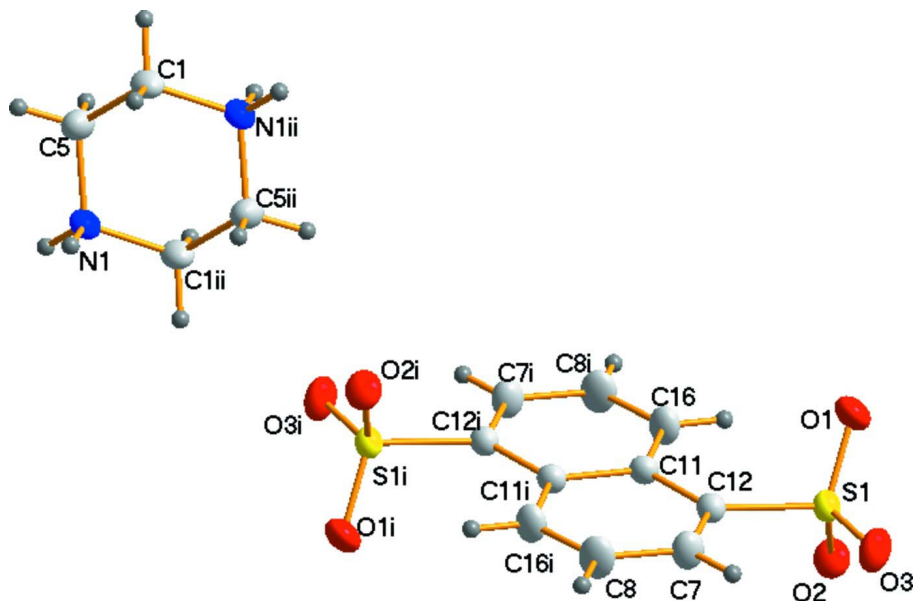


Figure 1

The molecular structure of the title compound with atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x + 2, -y, -z + 1$.

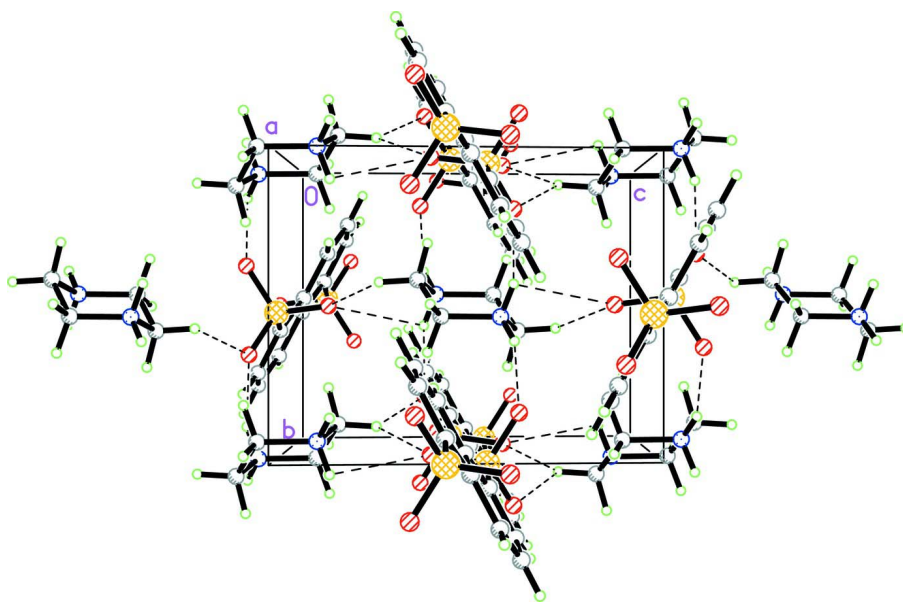


Figure 2

A view of the packing of the title compound along the a axis. Dashed lines indicate hydrogen bonds.

Piperazine-1,4-dium naphthalene-1,5-disulfonate

Crystal data

$C_4H_{12}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-}$

$M_r = 374.42$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 11.997(2) \text{ \AA}$

$b = 7.2959(15) \text{ \AA}$

$c = 9.1453(18) \text{ \AA}$

$\beta = 96.00(3)^\circ$

$V = 796.1 (3) \text{ \AA}^3$
 $Z = 2$
 $F(000) = 392$
 $D_x = 1.562 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

$\theta = 3.0\text{--}27.5^\circ$
 $\mu = 0.37 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Block, colorless
 $0.20 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Rigaku SCXmini
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 CCD_Profile_fitting scans
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.955$, $T_{\max} = 0.955$

7956 measured reflections
 1827 independent reflections
 1629 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -15 \rightarrow 15$
 $k = -9 \rightarrow 9$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.088$
 $S = 1.11$
 1827 reflections
 109 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.4026P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL*
 Extinction coefficient: 0

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	0.72018 (3)	0.02705 (6)	0.55200 (4)	0.02178 (13)
C11	0.94220 (13)	-0.0264 (2)	0.49266 (17)	0.0209 (3)
C12	0.86385 (13)	0.0911 (2)	0.55496 (17)	0.0213 (3)
C7	0.89809 (14)	0.2508 (2)	0.6239 (2)	0.0291 (4)
H7	0.8460	0.3258	0.6632	0.035*
C16	0.91084 (14)	-0.1936 (2)	0.4198 (2)	0.0287 (4)
H16	0.8360	-0.2294	0.4101	0.034*
C8	1.01178 (15)	0.3021 (3)	0.6358 (2)	0.0347 (4)
H8	1.0342	0.4115	0.6822	0.042*
N1	0.39695 (11)	0.03920 (19)	0.90988 (15)	0.0230 (3)

H1A	0.3451	0.1206	0.8730	0.028*
H1B	0.3762	-0.0722	0.8746	0.028*
C5	0.40092 (15)	0.0374 (3)	1.07288 (19)	0.0292 (4)
H5A	0.3293	-0.0036	1.1011	0.035*
H5B	0.4143	0.1607	1.1104	0.035*
C1	0.50731 (14)	0.0883 (3)	0.86030 (18)	0.0270 (4)
H1C	0.5256	0.2139	0.8882	0.032*
H1D	0.5027	0.0802	0.7540	0.032*
O1	0.67590 (11)	0.0023 (2)	0.39986 (15)	0.0384 (3)
O3	0.66605 (10)	0.17560 (17)	0.62410 (15)	0.0334 (3)
O2	0.72065 (10)	-0.14134 (17)	0.63779 (14)	0.0312 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0183 (2)	0.0221 (2)	0.0249 (2)	-0.00043 (14)	0.00176 (15)	0.00085 (15)
C11	0.0206 (8)	0.0213 (8)	0.0205 (8)	-0.0020 (6)	0.0011 (6)	-0.0019 (6)
C12	0.0196 (7)	0.0220 (8)	0.0221 (8)	-0.0016 (6)	0.0015 (6)	0.0005 (6)
C7	0.0253 (8)	0.0261 (9)	0.0362 (10)	0.0007 (7)	0.0047 (7)	-0.0093 (7)
C16	0.0225 (8)	0.0279 (9)	0.0357 (10)	-0.0072 (7)	0.0024 (7)	-0.0091 (8)
C8	0.0309 (9)	0.0290 (9)	0.0440 (11)	-0.0080 (7)	0.0032 (8)	-0.0176 (8)
N1	0.0229 (7)	0.0229 (7)	0.0221 (7)	0.0017 (5)	-0.0022 (5)	0.0011 (5)
C5	0.0282 (9)	0.0363 (10)	0.0235 (8)	0.0051 (7)	0.0047 (7)	0.0003 (7)
C1	0.0275 (8)	0.0321 (9)	0.0212 (8)	-0.0028 (7)	0.0012 (6)	0.0070 (7)
O1	0.0290 (7)	0.0556 (9)	0.0284 (7)	-0.0015 (6)	-0.0070 (5)	-0.0012 (6)
O3	0.0273 (6)	0.0267 (7)	0.0478 (8)	0.0040 (5)	0.0120 (6)	-0.0017 (6)
O2	0.0324 (7)	0.0230 (6)	0.0386 (7)	-0.0042 (5)	0.0051 (5)	0.0053 (5)

Geometric parameters (Å, °)

S1—O1	1.4477 (14)	C8—C16 ⁱ	1.359 (3)
S1—O3	1.4562 (13)	C8—H8	0.9300
S1—O2	1.4574 (13)	N1—C5	1.486 (2)
S1—C12	1.7834 (16)	N1—C1	1.487 (2)
C11—C16	1.422 (2)	N1—H1A	0.9000
C11—C11 ⁱ	1.432 (3)	N1—H1B	0.9000
C11—C12	1.434 (2)	C5—C1 ⁱⁱ	1.512 (2)
C12—C7	1.367 (2)	C5—H5A	0.9700
C7—C8	1.408 (2)	C5—H5B	0.9700
C7—H7	0.9300	C1—C5 ⁱⁱ	1.512 (2)
C16—C8 ⁱ	1.359 (3)	C1—H1C	0.9700
C16—H16	0.9300	C1—H1D	0.9700
O1—S1—O3	113.07 (8)	C7—C8—H8	119.6
O1—S1—O2	113.12 (8)	C5—N1—C1	111.82 (13)
O3—S1—O2	111.13 (8)	C5—N1—H1A	109.3
O1—S1—C12	107.70 (8)	C1—N1—H1A	109.3
O3—S1—C12	105.90 (8)	C5—N1—H1B	109.3

O2—S1—C12	105.28 (8)	C1—N1—H1B	109.3
C16—C11—C11 ⁱ	118.75 (18)	H1A—N1—H1B	107.9
C16—C11—C12	123.17 (15)	N1—C5—C1 ⁱⁱ	110.87 (14)
C11 ⁱ —C11—C12	118.07 (18)	N1—C5—H5A	109.5
C7—C12—C11	121.01 (15)	C1 ⁱⁱ —C5—H5A	109.5
C7—C12—S1	118.27 (13)	N1—C5—H5B	109.5
C11—C12—S1	120.66 (12)	C1 ⁱⁱ —C5—H5B	109.5
C12—C7—C8	120.27 (16)	H5A—C5—H5B	108.1
C12—C7—H7	119.9	N1—C1—C5 ⁱⁱ	111.37 (14)
C8—C7—H7	119.9	N1—C1—H1C	109.4
C8 ⁱ —C16—C11	121.18 (16)	C5 ⁱⁱ —C1—H1C	109.4
C8 ⁱ —C16—H16	119.4	N1—C1—H1D	109.4
C11—C16—H16	119.4	C5 ⁱⁱ —C1—H1D	109.4
C16 ⁱ —C8—C7	120.71 (16)	H1C—C1—H1D	108.0
C16 ⁱ —C8—H8	119.6		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O2 ⁱⁱⁱ	0.90	1.91	2.7357 (19)	153
N1—H1B \cdots O3 ^{iv}	0.90	1.91	2.7670 (19)	159

Symmetry codes: (iii) $-x+1, y+1/2, -z+3/2$; (iv) $-x+1, y-1/2, -z+3/2$.