

## 3,6-Di-2-pyridinio-1,2,4,5-tetrazine diperchlorate

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The structure of the title compound,  $C_{12}H_{10}N_6^{2+} \cdot 2ClO_4^-$ , has a crystallographic center of symmetry. The pyridinium ring makes a dihedral angle of  $26.4(3)^\circ$  with the mean plane of the central 1,2,4,5-tetrazine plane. The perchlorate anions link the cations to form a chain structure through  $C-H \cdots O$  close contacts and  $N-H \cdots O$  hydrogen bonds.

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## Key indicators

Single-crystal X-ray study

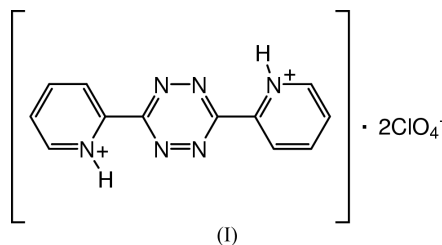
 $T = 293\text{ K}$ Mean  $\sigma(C-C) = 0.004\text{ \AA}$  $R$  factor = 0.037 $wR$  factor = 0.116

Data-to-parameter ratio = 11.4

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

## Comment

3,6-Di-2-pyridyl-1,2,4,5-tetrazine (Dptz) has been applied as a coordinative  $\pi$ -acceptor moiety in the study of photophysical and redox properties of transition metal complexes, and a bridging building block for supramolecular assemblies (Campos-Fernandez *et al.*, 1999; Bu *et al.*, 2000). This type of aromatic compounds also exhibit proton-sponge properties (Staab & Saupe, 1988; Robertson *et al.*, 1998), which can act as external proton acceptors through formation of  $N-H \cdots Y$  hydrogen bonds. In the present paper, we report the crystal structure of the diprotonated salt of Dptz, namely 3,6-di-2-pyridinio-1,2,4,5-tetrazine, (I).



There is half a molecule in the asymmetric unit and the other half is inversion related (Fig. 1). The bond distances and angles (Table 1) agree with those of the structure of Dptz (Klein *et al.*, 1998). The structure shows the expected *trans* configuration for the two pyridine groups. The pyridine ring makes a dihedral angle of  $26.4(3)^\circ$  with the mean plane of the central 1,2,4,5-tetrazine plane (the value in the structure of Dptz molecule is  $19.1^\circ$ ).

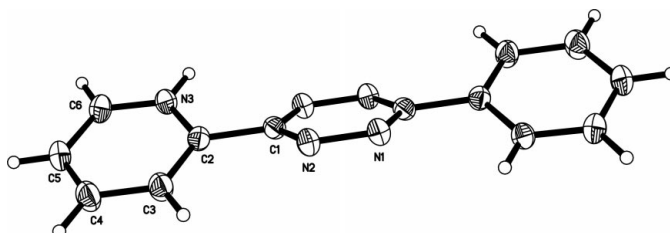


Figure 1

ORTEP (Johnson, 1976) view of diprotonated Dptz shown with 30% probability ellipsoids.

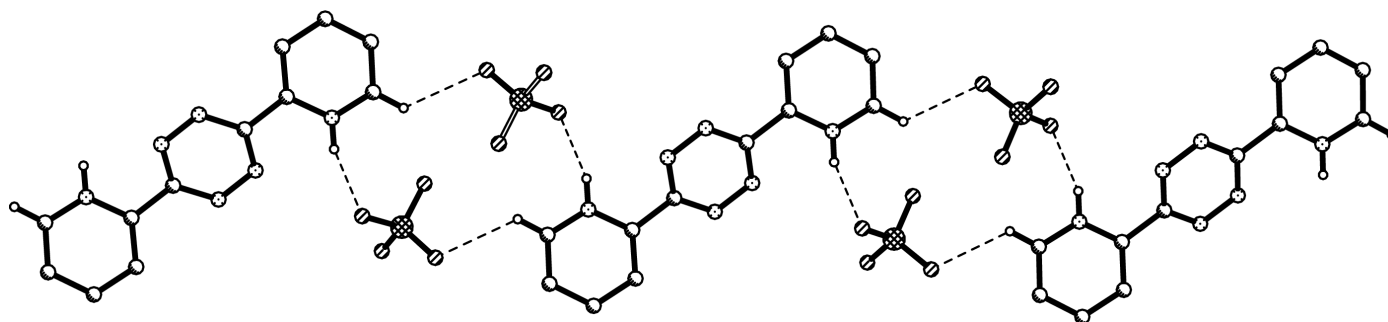


Figure 2

View of the one-dimensional chain in the crystal (irrelevant H atoms have been omitted for clarity).

The perchlorate anions act as bridges to link the cations through hydrogen bonds, forming a chain structure as shown in Fig. 2. The C(N)···O and H···O separations, and the bond angles are listed in Table 2, which are in the normal range for weak interactions (Sasada, 1984; Desiraju, 1991). The cations are stacked in the *a* direction with the closest approach between the pyridine and tetrazine ring of *ca* 4.0 Å, indicating no significant  $\pi$ ··· $\pi$  stacking interactions.

## Experimental

Dptz was prepared following the literature procedure of Kaim & Kohlmann (1987). Crystals of (I) were obtained by slow diffusion of diethyl ether into an acetonitrile solution of Dptz in the presence of HClO<sub>4</sub>.

### Crystal data

C <sub>12</sub> H <sub>10</sub> N <sub>6</sub> <sup>2+</sup> ·2ClO <sub>4</sub> <sup>-</sup>	Z = 1
<i>M<sub>r</sub></i> = 437.16	<i>D<sub>x</sub></i> = 1.736 Mg m <sup>-3</sup>
Triclinic, P1̄	Mo Kα radiation
<i>a</i> = 5.6592 (9) Å	Cell parameters from 1718 reflections
<i>b</i> = 8.5549 (13) Å	$\theta$ = 2.4–25.0°
<i>c</i> = 8.7070 (14) Å	$\mu$ = 0.45 mm <sup>-1</sup>
$\alpha$ = 87.454 (3)°	<i>T</i> = 293 (2) K
$\beta$ = 85.360 (3)°	Prism, red
$\gamma$ = 85.004 (3)°	0.30 × 0.20 × 0.10 mm
<i>V</i> = 418.27 (11) Å <sup>3</sup>	

### Data collection

Bruker SMART 1000 diffractometer	1454 independent reflections
$\omega$ scans	1339 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan [SAINT (Bruker, 1998) and SADABS (Sheldrick, 1997)]	<i>R</i> <sub>int</sub> = 0.015
<i>T</i> <sub>min</sub> = 0.877, <i>T</i> <sub>max</sub> = 0.957	$\theta$ <sub>max</sub> = 25.0°
1726 measured reflections	<i>h</i> = -5 → 6
	<i>k</i> = -7 → 10
	<i>l</i> = -9 → 10

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0934P)^2 + 0.2332P]$
<i>R</i> ( <i>F</i> ) = 0.037	where $P = (F_o^2 + 2F_c^2)/3$
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.117	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
<i>S</i> = 0.89	$\Delta\rho$ <sub>max</sub> = 0.36 e Å <sup>-3</sup>
1454 reflections	$\Delta\rho$ <sub>min</sub> = -0.26 e Å <sup>-3</sup>
127 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

N1—N2	1.316 (2)	N3—C6	1.328 (3)
N1—C1 <sup>i</sup>	1.334 (3)	N3—C2	1.344 (3)
N2—C1	1.334 (3)	C1—N1 <sup>i</sup>	1.334 (3)

N2—N1—C1 <sup>i</sup>	117.02 (17)	N2—C1—C2	117.15 (18)
N1—N2—C1	116.69 (17)	N3—C2—C3	119.29 (19)
C6—N3—C2	122.60 (19)	N3—C2—C1	116.83 (18)
N1 <sup>i</sup> —C1—N2	126.29 (18)	N3—C6—C5	119.9 (2)
N1 <sup>i</sup> —C1—C2	116.56 (18)		

Symmetry code: (i) 2 - *x*, 1 - *y*, 1 - *z*.

Table 2

Hydrogen-bonding 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>
N3—H3a···O4	0.86	1.98	2.800 (3)	159
C6—H6a···O3 <sup>i</sup>	0.93	2.50	3.149 (4)	127

Symmetry code: (i) -*x*, 1 - *y*, 2 - *z*.

H atoms were located by geometry and constrained.

Data collection: SMART (Bruker, 1998); cell refinement and data reduction: SAINT (Bruker, 1998); structure solution: SHELXS97 (Sheldrick, 1997); program structure refinement: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Bruker, 1998).

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