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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.049

wR factor = 0.130

Data-to-parameter ratio = 16.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Bis[(5*RS*,11*RS*)-2,8-dimethyl-5,10-methano-
5,6,11,12-tetrahydrodibenzo[*b,f*][1,5]-
diazocine-5-ium dihydrogen phosphate]
tris(phosphoric acid) methanol solvate**

In the title compound, $2\text{C}_{17}\text{H}_{19}\text{N}_2^+ \cdot 2\text{H}_2\text{PO}_4^- \cdot 3\text{H}_3\text{PO}_4 \cdot \text{CH}_3\text{OH}$, Tröger base, phosphoric acid and methanol are included in the crystal structure, the asymmetric unit of which contains three protonated acid units. The structure includes hydrophilic layers of dihydrogen phosphate anions, phosphoric acid and methanol which are interconnected by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. These layers alternate with the more hydrophobic Tröger base. Each Tröger base acts as a proton donor in an $\text{N}-\text{H} \cdots \text{O}$ hydrogen bond.

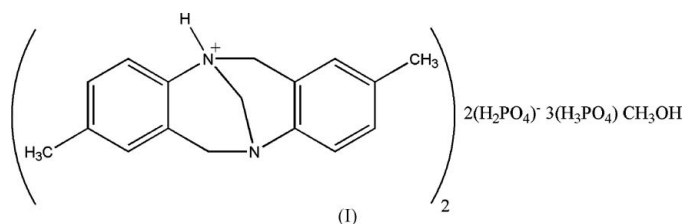
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Comment

Tröger base (Tröger, 1887), 2,8-dimethyl-6*H*,12*H*-5,11-methanodibenzo[*b,f*][1,5]diazocine, was the first chiral heterocyclic amine for which the chirality is due to the presence of two stereogenic N atoms. The chiral nature of Tröger base was first recognized by Prelog & Wieland (1944) and confirmed by those workers by optical resolution of the racemate.



Tröger base is an interesting rigid polycyclic diamine which has a long history. Recently, it has received attention as a template for studies of molecular recognition and inclusion (Vögtle, 1992; Bag, 1995; Demeunynck & Tatibouet, 1999; Kim *et al.*, 1998). However, very little has been done to exploit Tröger base as a chiral ligand. Only a few metal complexes of Tröger base have been reported and their use as catalysts in the hydrosilylation of alkynes documented (Harmata *et al.*, 1996; Goldberg & Alper, 1995).

The synthesis of enantiomerically pure Tröger base has been performed by an asymmetric transformation and other template-based approaches (Wilén & Qi, 1991; Maitra *et al.*, 1995).

We have prepared the title compound, (I), of Tröger base in the context of a project on new materials with nonlinear optical properties. The molecular conformation of (I) is illustrated in Fig. 1.

Tröger base in the title compound is protonated on atom N5. The lengths of the C–N bonds are in the range 1.427 (3)–1.514 (3) Å, similar to those observed in the structure of free Tröger base (Larson & Wilcox, 1986). The intramolecular dihedral angle between the two planes of the aromatic rings is

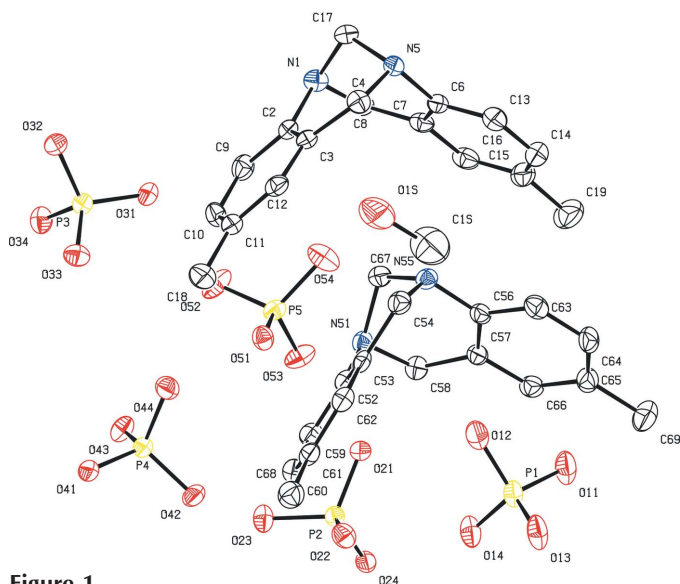


Figure 1
The independent components of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for the sake of clarity.

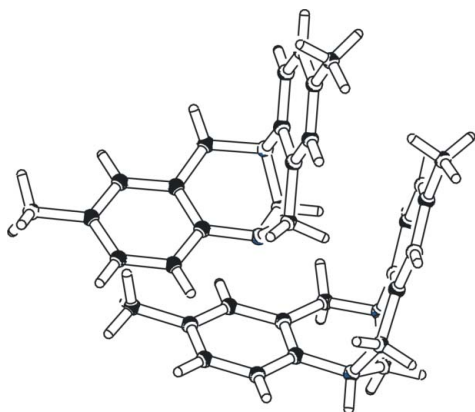


Figure 2
Part of the crystal structure of (I), showing the formation of cation layers. Hydrogen bonds are indicated by dashed lines.

82.07 (9)° for the first molecule of Tröger base in the independent unit and 82.55 (8)° for the second. These values are smaller than similar dihedral angles in the structure of free Tröger base [92.85 (17) and 97.38 (16)°].

The crystal structure of (I) involves alternating layers of Tröger base cations (Fig. 2) and layers containing phosphoric acid, dihydrogen phosphates and methanol connected by an extensive system of O—H...O hydrogen bonds (Table 2 and Fig. 3). These hydrophilic layers and Tröger bases are connected by N—H...O hydrogen bonds (Table 2 and Fig. 4).

Experimental

Tröger base was prepared by condensation of formaldehyde and *p*-toluidine, purified, and characterized as a yellow powder by a procedure described in the literature (Sucholeiki *et al.*, 1988). Crystals of the title compound were obtained from a solution of Tröger base (0.5 g) and phosphoric acid (1 ml) in methanol (5 ml). The solution was left to crystallize at room temperature for several weeks. The

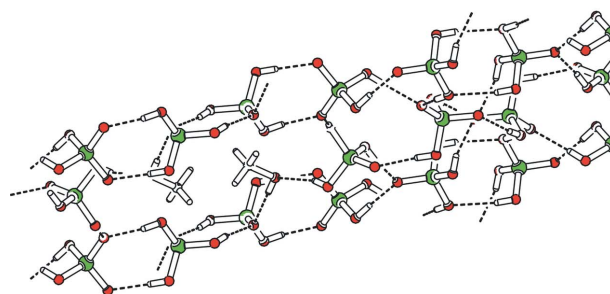


Figure 3
Part of the crystal structure of (I), showing the formation of anion layers along [210].

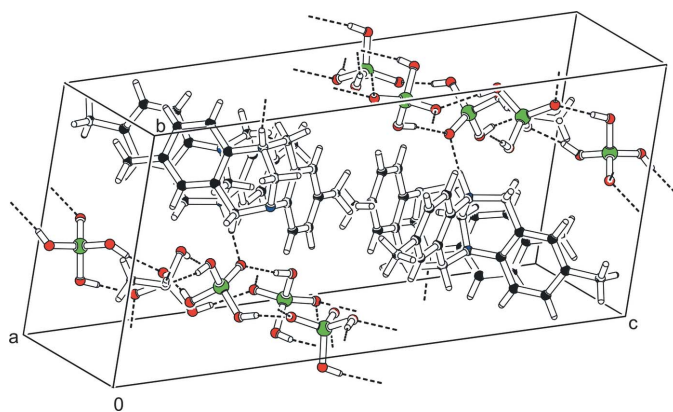


Figure 4
A packing diagram of the structure of (I). Hydrogen bonds are indicated by dashed lines.

colourless crystals obtained were filtered off, washed with methanol and dried in a vacuum desiccator over KOH.

Crystal data

$2C_{17}H_{19}N_2^+ \cdot 2H_2O_4P^- \cdot 3H_3O_4P^- \cdot CH_4O$
 $M_r = 1022.68$
 Triclinic, $P\bar{1}$
 $a = 10.1330$ (2) Å
 $b = 10.3690$ (2) Å
 $c = 22.4040$ (6) Å
 $\alpha = 76.9690$ (13)°
 $\beta = 88.3810$ (14)°
 $\gamma = 88.3660$ (15)°
 $V = 2291.84$ (9) Å³

$Z = 2$
 $D_x = 1.482$ (1) Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 10003 reflections
 $\theta = 1.0$ –27.5°
 $\mu = 0.28$ mm⁻¹
 $T = 150$ (2) K
 Block, colourless
 0.15 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω and φ scans
 Absorption correction: none
 42017 measured reflections
 10505 independent reflections

6499 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.053$
 $\theta_{max} = 27.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -29 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.130$
 $S = 1.03$
 10505 reflections
 650 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.239P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.38$ e Å⁻³
 $\Delta\rho_{min} = -0.46$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

P2—O21	1.5086 (17)	N5—C6	1.473 (3)
P2—O24	1.5097 (18)	N5—C17	1.511 (3)
P2—O22	1.559 (2)	C2—C3	1.390 (4)
P2—O23	1.562 (2)	C2—N1	1.441 (3)
P1—O13	1.489 (2)	N1—C17	1.435 (3)
P1—O11	1.538 (2)	N1—C8	1.473 (3)
P1—O14	1.543 (2)	C8—C7	1.504 (4)
P1—O12	1.550 (2)	C6—C7	1.393 (4)
C4—C3	1.507 (3)		
N5—C4—C3	110.9 (2)	C2—N1—C8	112.6 (2)
C6—N5—C4	114.2 (2)	N1—C8—C7	111.8 (2)
C6—N5—C17	110.9 (2)	C2—C3—C4	121.7 (2)
C4—N5—C17	107.5 (2)	C7—C6—N5	119.9 (2)
C6—N5—H5	104 (2)	N1—C17—N5	109.40 (19)
C4—N5—H5	112.0 (19)	C6—C7—C8	121.7 (2)
C3—C2—N1	120.9 (2)		

Table 2
Hydrogen-bond 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>
O33—H33...O41 ⁱ	0.79 (4)	1.74 (4)	2.506 (3)	162 (5)
O32—H32...O42 ⁱⁱ	0.95 (5)	1.54 (5)	2.490 (2)	172 (5)
O44—H44...O51	0.82 (4)	1.82 (4)	2.634 (3)	172 (4)
O23—H23...O42	0.76 (3)	1.89 (3)	2.642 (3)	177 (3)
O34—H34...O32 ⁱⁱⁱ	0.79 (3)	2.03 (3)	2.811 (3)	174 (3)
O43—H43...O41 ⁱ	0.71 (3)	1.96 (3)	2.661 (3)	171 (4)
O53—H53...O21	0.83 (3)	1.71 (4)	2.535 (3)	172 (4)
N51—H51...O51	1.06 (3)	1.65 (3)	2.700 (3)	174 (3)
O52—H52...O31	0.85 (4)	1.71 (5)	2.554 (3)	172 (4)
O14—H14...O24	0.79 (3)	1.77 (4)	2.565 (3)	177 (4)
N5—H5...O24 ^{iv}	0.92 (3)	1.74 (3)	2.648 (3)	169 (3)
O22—H22...O31 ^v	0.88 (3)	1.75 (3)	2.627 (3)	177 (3)
O54—H54...O15	0.70 (4)	1.88 (4)	2.551 (3)	163 (5)
O12—H12...O21	0.82 (4)	1.75 (4)	2.561 (3)	170 (5)
O11—H11...O13 ^{vi}	0.71 (4)	1.84 (4)	2.543 (3)	171 (5)
O15—H15...O13 ⁱⁱ	0.80 (4)	1.94 (4)	2.743 (3)	176 (5)

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

H atoms attached to C atoms were calculated in geometrically idealized positions, with $Csp^3-H = 0.96$ Å for methyl, $C-H = 0.97$ Å

for methylene and $Csp^2-H = 0.93$ Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$. H atoms attached to O and N atoms were located in difference Fourier maps and refined isotropically.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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