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# 1,7-Dihydro-1,4,7,10-tetraazacyclododecanephosphine oxide iodide

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The title compound, $C_8H_{18}N_4OP^+\cdot I^-$ or [$H_2$cyclenPO][I], contains a five-coordinate P atom arranged in a slightly distorted trigonal bipyramid. The asymmetric unit contains half the cyclen moiety of the H~2~cyclenPO unit and two distinct iodide positions. The full molecule can be symmetry generated around the P atom using the symmetry code $\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{5}{3}-z$. The P—N bond length in the equatorial plane is 1.656 (5) Å and the apical P—N interaction is much longer, 1.891 (4) Å. The cyclen moieties are linked together *via* N—H···O hydrogen bonds and form a spiral chain along [001]. Crystallographically, there are two distinct anion sites, both in special positions, one of them with partial occupancy. One anion site may participate in an extremely weak hydrogen bond, linking the cyclen spiral chains into a pseudo-hexagonal three-dimensional array.

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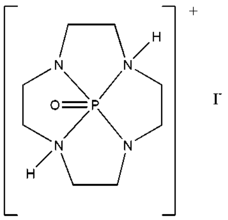
**Key indicators**

Single-crystal X-ray study
$T$ = 213 K
Mean $\sigma$(C–C) = 0.010 Å
Disorder in solvent or counterion
$R$ factor = 0.047
$wR$ factor = 0.116
Data-to-parameter ratio = 18.1

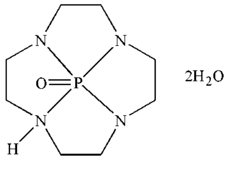
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

Cyclen chemistry is extensive, with 431 hits in the November 2002 release of the Cambridge Structural Database (CSD; Allen, 2002). However, only one cyclen phosphine oxide is described in the database, namely cyclenphosphine oxide dihydrate, (II) (Oget *et al.*, 1999). Compound (II) was first described in a patent (Richman, 1976) and the solution structure elucidated by NMR methods (Richman & Kubale, 1983). Although other cyclen phosphine chalcogenide derivatives have been synthesized (Oget *et al.*, 1998), no structural information has been reported.



(I)



(II)

Compound (I) is a hydrolytic by-product formed during reactions of cyclenphosphorane (Gupta *et al.*, 1998). The title compound, (I), is similar to (II). (I) is protonated, cationic and charge balanced by an iodide anion (see Fig. 1). The P atom lies on a special position (Wyckoff position *e*, point symmetry 2) and the other half of the cation is symmetry-generated. The P atom is five-coordinate and forms a slightly distorted trigonal bipyramid (tbp). The equatorial plane atoms [N2, O1, N2$^{i}$ and P1; symmetry code: (i) $\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{5}{3}-z$] are exactly coplanar. The distortion from tbp can be seen in the axial and equatorial N—P—N angles [167.1 (3), 123.4 (4) and 118.3 (2)°]. The P—N distances show that the equatorial N

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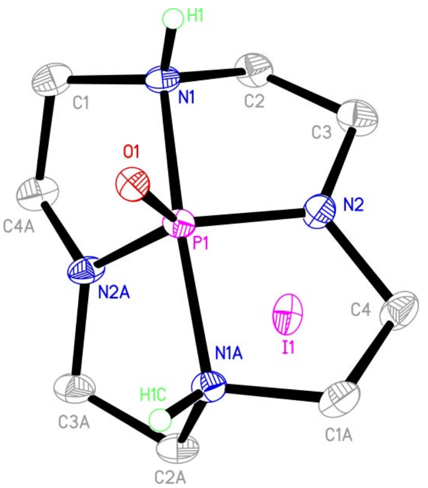

**Figure 1**
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Only one of the iodide positions is shown.

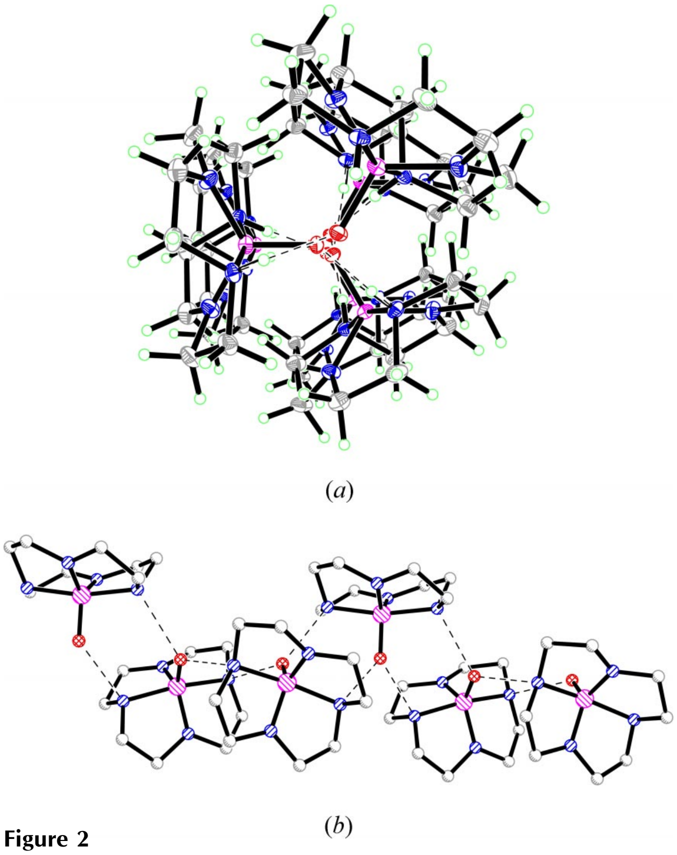

**Figure 2**
(*a*) A head-on view of the hydrogen-bonded network of the cyclen units. Ellipsoids are drawn at the 30% probability level. (*b*) A ball-and-stick side view of the hydrogen bonding between the cyclen units, showing the spiral chain.

atoms are bonded to the phosphorus [P1—N2 and P1—N2$^{\rm i}$ = 1.656 (5) Å]. The apical P—N distances [P1—N1 and P1—Ni$^{\rm i}$ = 1.891 (4) Å] are longer than that of a single P—N bond. They are considerably shorter than the sum of the van der Waals radii (3.35 Å) and indicate a strong coordination of the central phosphorus by these N atoms. The elongation of the apical P—N bond in a tbp is expected, and this bond lengthening has been reported previously with a range of P—N$_{\rm apical}$ distances of 1.8 to 2.11 Å [*e.g.* CSD refcode YAFDUE (Khasnis *et al.*, 1992), LOBYUW (Gupta *et al.*, 1999) and GOCPUJ (Oget at al., 1999)]. Atoms N1 and N1$^{\rm i}$ are both protonated and the H atom was located in a difference map. Iodide anions, totalling nine per unit cell for charge balance, are in two crystallographically distinct sites, both in special positions. I1 is located at Wyckoff position *b* (point symmetry 32) with full occupancy, while I1′ is located at position *d* (point symmetry 2) with 2/3 occupancy; these occupancy factors are confirmed by free refinement.

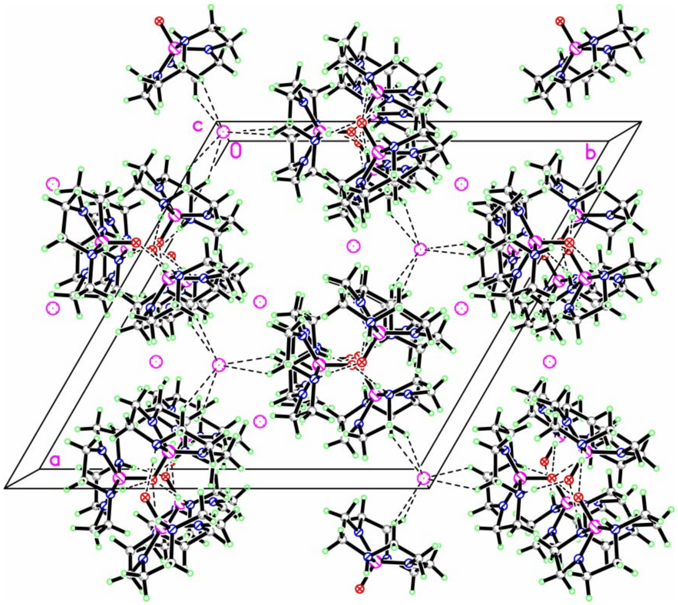

**Figure 3**
A ball-and-stick packing diagram of (I). The cell is shown. Very weak H$\cdots$I interactions are indicated by dashed lines outlining the pseudo-hexagonal shape formed by the cyclen chains and one of the anion positions.

The cyclen phosphine oxide moiety is twisted about the N1—P1—N1$^{\rm i}$ plane. The amido H atoms are oriented to either side of this plane (0.41 and −0.41 Å). This produces a slight helical distortion of the cyclen moiety. This helical distortion can also be seen in bis(borane)cyclenphosphorane (Dupart *et al.*, 1985). The absolute configuration of chiral (I) could not be determined reliably and (I) was refined as a racemic twin.

The extended solid state structure generated by intermolecular interactions presents an interesting picture:

(i) N—H$\cdots$O hydrogen bonding. There are two of these interactions per cyclen moiety, linking the cyclen PO units into a spiral chain that runs parallel to [001]. This is shown in Figs. 2(*a*) and 2(*b*). Distances and angles are given in Table 1.

(ii) C—H$\cdots$I interactions. These 'interactions' should be considered extremely weak or almost non-existent. They are at the furthest limit of reported weak C—H$\cdots$*X* interactions (Desiraju & Steiner, 2001). However, they may have an influence on the supramolecular association, by linking the spiral cyclen chains into a pseudo-hexagonal array (three H$_2$cyclenPO$^+$ cations and three I$^-$ anions) (Fig. 3). The space between these networked molecules is occupied by the symmetry-related unassociated iodide position. This leaves large voids between the spiral chains, *ca* 94 Å$^3$ in the asymmetric unit.

## Experimental

Compound (I) was synthesized as a hydrolytic by-product from reactions of cyclenphosphorane (Gupta *et al.*, 1998). Colorless crystals were obtained from a $CHCl_3$ solution, yield 95%. IR (cm$^{-1}$, KBr pellet): 3100 (*w*), 2935 (*vs*), 2856 (*s*), 1460 (*s*), 1392 (*vs*), 1232 (*s*), 1141 (*vs*), 1088 (*vs*), 746 (*m*), 627 (*s*).

### Crystal data

$C_8H_{18}IN_4OP$
$M_r = 344.13$
Trigonal, $R32$
$a = 19.327$ (3) Å
$c = 10.052$ (2) Å
$V = 3251.7$ (10) Å$^3$
$Z = 9$
$D_x = 1.582$ Mg m$^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 3934 reflections
$\theta = 2.3\text{–}23.5°$
$\mu = 2.31$ mm$^{-1}$
$T = 213$ (2) K
Parallelepiped, colorless
0.30 × 0.20 × 0.20 mm

### Data collection

Burker/Siemens SMART 1K CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
$T_{\min} = 0.522$, $T_{\max} = 0.628$
14029 measured reflections

1324 independent reflections
1260 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 25.4°$
$h = -23 \rightarrow 16$
$k = -21 \rightarrow 23$
$l = -12 \rightarrow 11$

### Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.117$
$S = 1.14$
1324 reflections
73 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2 + 14.9452P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.86$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.86$ e Å$^{-3}$

### Table 1

Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| C2—H2$B$···I1 | 0.98 | 3.23 | 4.023 (6) | 140 |
| N1—H1···O1$^{\rm ii}$ | 0.86 | 1.91 | 2.769 (5) | 176 |

Symmetry code: (ii) $\frac{5}{3} - x + y, \frac{4}{3} - x, \frac{1}{3} + z$.

H atoms were positioned geometrically and refined using a riding model, with $U_{\rm iso}$ values constrained to be $1.2U_{\rm eq}$ of the carrier atom. Atom H1 was located in a difference map. The distance was restrained and the $U_{\rm iso}$ value constrained to be $1.2U_{\rm eq}$ of carrier atom N1. The structure was refined as a racemic twin.

Data collection: *SMART* (Bruker, 1997–1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *XS* in *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *XL* in *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *XCIF* in *SHELXTL*.

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