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3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphospiro[5.5]undecane-3,9-dione

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Key indicators: single-crystal X-ray study; $T = 185$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.031; wR factor = 0.069; data-to-parameter ratio = 13.6.

In the title compound, $\text{C}_5\text{H}_8\text{Cl}_2\text{O}_6\text{P}_2$, the two six-membered rings display chair conformations. The $\text{P}=\text{O}$ bond distances are 1.444 (2) and 1.446 (2) Å. Weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds are present in the crystal structure.

Related literature

For applications of pentaerythritol diphosphonate compounds, see: Granzow (1981); Tanabe *et al.* (2005). For details of the preparation of the title compound, see: Li *et al.* (2002). For related compounds, see: Heinemann *et al.* (1994); Zhang *et al.* (2006). For bond-length, see: Allen *et al.* (1987); Elnagar *et al.* (2000).



Experimental

Crystal data

 $\text{C}_5\text{H}_8\text{Cl}_2\text{O}_6\text{P}_2$ $M_r = 296.95$ Orthorhombic, $P2_12_12_1$ $a = 6.0630$ (5) Å $b = 12.7384$ (10) Å $c = 13.4338$ (10) Å $V = 1037.53$ (14) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.94$ mm⁻¹ $T = 185$ K

0.12 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD 1000 area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2001)

 $T_{\min} = 0.896$, $T_{\max} = 0.929$

5317 measured reflections

1849 independent reflections

1662 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.036$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$ $wR(F^2) = 0.069$ $S = 1.00$

1849 reflections

136 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Absolute structure: Flack (1983),

747 Friedel pairs

Flack parameter: 0.18 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C1}-\text{H1A}\cdots\text{O5}^i$	0.99	2.34	3.214 (4)	147
$\text{C1}-\text{H1B}\cdots\text{O6}^{ii}$	0.99	2.31	3.252 (4)	159
$\text{C4}-\text{H4B}\cdots\text{O5}^i$	0.99	2.36	3.260 (4)	150

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5060).

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supporting information

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3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dione**Zhao-Shun Zhan, Hong Wang, Li-Ping Ding, Chun-Mei Dong and Cai-Ying Sun****S1. Comment**

Studies of pentaerythritol diphosphonate compounds have been significant interested. On one hand, the compounds have been reported to act as one of the most important reaction intermediates of fire retardant agents (Tanabe *et al.*, 2005). On the other hand, it seems to be a good candidate in modifying the stability of polymers (Granzow, 1981). The findings have triggered the development of new flame retardant materials. As an extension of the work on the structural characterization of pentaerythritol diphosphonate compounds, the preparation and crystal structure of the title compound, (I), is proposed here.

The asymmetric unit of (I) contain a spiro[5.5]undecane molecule (Fig. 1). Several compounds with similar structures have been reported previously (Heinemann *et al.*, 1994; Zhang *et al.*, 2006). The bond lengths and angles are within normal ranges (Allen *et al.*, 1987; Elnagar *et al.*, 2000). The six-membered rings of (I) have the chair conformation consistent with the steric difference in this conformation between opposite ends of the molecule. In addition, the C1—C3—C2 and C4—C3—C5 angles are in the range of 109.4 (3)–109.2 (3)°, the P—Cl bond lengths are 2.0050 (14) and 2.0047 (13) Å, respectively. In the crystal structure of (I), The non-classic C—H···O hydrogen bonds ranging from 3.099 (4) to 3.260 (4) Å contributed to the stability of the crystal packing.

S2. Experimental

The title compound was prepared by reaction of pentaerythritol with phosphorus oxychloride in acetonitrile according to the reported procedures (Li *et al.*, 2002). Crystals were produced at the bottom of the vessel on slow evaporation of acetic acid solution.

S3. Refinement

All H atoms were placed geometrically with C—H = 0.99 Å and refined using a riding atom model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

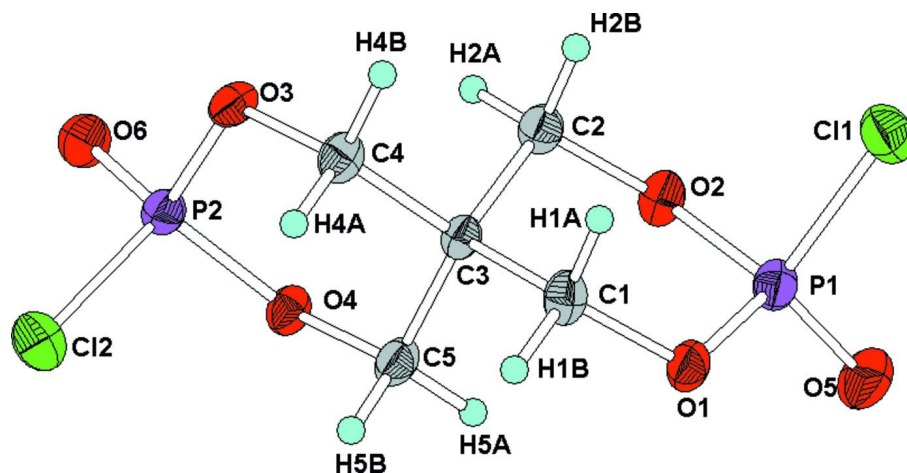


Figure 1

A view of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

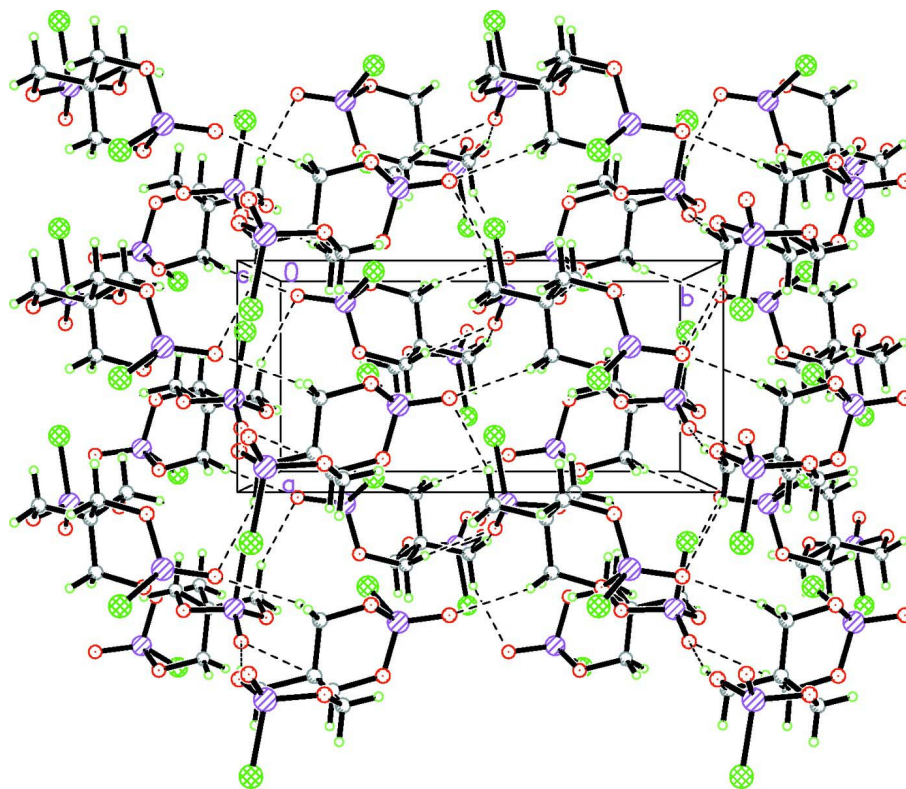


Figure 2

The crystal packing through C—H...O interactions along the *c* axis

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Crystal data

$C_5H_8Cl_2O_6P_2$
 $M_r = 296.95$

Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab

$a = 6.0630$ (5) Å
 $b = 12.7384$ (10) Å
 $c = 13.4338$ (10) Å
 $V = 1037.53$ (14) Å³
 $Z = 4$
 $F(000) = 600$
 $D_x = 1.901$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 2823 reflections
 $\theta = 2.2\text{--}25.0^\circ$
 $\mu = 0.94$ mm⁻¹
 $T = 185$ K
 Block, colorless
 $0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD 1000 area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2001)
 $T_{\min} = 0.896$, $T_{\max} = 0.929$

5317 measured reflections
 1849 independent reflections
 1662 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 25.1^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -5 \rightarrow 7$
 $k = -14 \rightarrow 15$
 $l = -14 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.069$
 $S = 1.00$
 1849 reflections
 136 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
 $w = 1/[\sigma^2(F_o^2) + (0.0283P)^2 + 0.5846P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.27$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³
 Absolute structure: Flack (1983), 747 Friedel
 pairs
 Absolute structure parameter: 0.18 (10)

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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
P2	0.86704 (16)	0.68037 (6)	0.19061 (7)	0.0195 (2)
P1	0.61011 (17)	0.94037 (7)	0.51917 (6)	0.0225 (2)
Cl2	1.00827 (16)	0.75305 (7)	0.07460 (7)	0.0322 (2)
Cl1	0.28767 (15)	0.96781 (7)	0.53971 (7)	0.0299 (2)
O4	0.9665 (4)	0.73565 (16)	0.28413 (16)	0.0197 (5)
O2	0.6224 (4)	0.82146 (16)	0.48872 (15)	0.0218 (5)
O6	0.8993 (4)	0.56810 (17)	0.18897 (18)	0.0274 (6)
O3	0.6190 (4)	0.71416 (16)	0.18620 (16)	0.0206 (5)

O1	0.6715 (4)	1.00446 (16)	0.42462 (16)	0.0227 (6)
O5	0.7431 (5)	0.96565 (19)	0.60521 (16)	0.0338 (6)
C3	0.6534 (6)	0.8561 (2)	0.3088 (2)	0.0170 (7)
C5	0.9032 (6)	0.8438 (2)	0.3065 (3)	0.0208 (8)
H5A	0.9656	0.8912	0.2553	0.025*
H5B	0.9652	0.8644	0.3718	0.025*
C4	0.5581 (6)	0.8229 (2)	0.2084 (2)	0.0198 (8)
H4A	0.3955	0.8295	0.2098	0.024*
H4B	0.6152	0.8697	0.1555	0.024*
C1	0.5966 (6)	0.9720 (2)	0.3254 (2)	0.0211 (7)
H1A	0.6694	1.0155	0.2740	0.025*
H1B	0.4353	0.9822	0.3198	0.025*
C2	0.5455 (6)	0.7897 (3)	0.3905 (2)	0.0207 (8)
H2A	0.3833	0.7978	0.3870	0.025*
H2B	0.5810	0.7147	0.3796	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P2	0.0192 (5)	0.0181 (4)	0.0211 (5)	−0.0002 (4)	0.0003 (4)	−0.0033 (4)
P1	0.0263 (5)	0.0223 (5)	0.0189 (5)	−0.0018 (4)	0.0020 (4)	−0.0028 (4)
Cl2	0.0331 (5)	0.0376 (5)	0.0259 (5)	−0.0039 (5)	0.0073 (4)	0.0002 (4)
Cl1	0.0282 (5)	0.0299 (5)	0.0317 (5)	0.0023 (4)	0.0074 (4)	−0.0002 (4)
O4	0.0187 (13)	0.0183 (12)	0.0221 (12)	0.0044 (11)	−0.0028 (10)	−0.0046 (10)
O2	0.0295 (13)	0.0182 (11)	0.0178 (12)	0.0025 (11)	−0.0017 (11)	0.0003 (9)
O6	0.0283 (14)	0.0192 (12)	0.0346 (14)	0.0004 (11)	0.0046 (13)	−0.0042 (11)
O3	0.0205 (12)	0.0169 (11)	0.0245 (12)	−0.0013 (10)	−0.0035 (12)	−0.0037 (10)
O1	0.0307 (15)	0.0169 (11)	0.0206 (12)	−0.0025 (11)	0.0042 (11)	−0.0037 (10)
O5	0.0393 (16)	0.0398 (15)	0.0223 (12)	−0.0063 (14)	−0.0051 (13)	−0.0065 (11)
C3	0.0198 (18)	0.0146 (15)	0.0166 (16)	0.0006 (13)	−0.0007 (15)	−0.0015 (13)
C5	0.0248 (19)	0.0164 (16)	0.0212 (18)	−0.0009 (15)	−0.0002 (17)	−0.0046 (14)
C4	0.0219 (19)	0.0151 (16)	0.0223 (19)	0.0042 (15)	−0.0024 (15)	−0.0015 (14)
C1	0.028 (2)	0.0183 (17)	0.0167 (17)	0.0027 (16)	0.0007 (16)	0.0000 (14)
C2	0.024 (2)	0.0189 (18)	0.0196 (18)	0.0002 (15)	0.0002 (15)	−0.0014 (14)

Geometric parameters (Å, °)

P2—O6	1.444 (2)	C3—C5	1.523 (5)
P2—O4	1.561 (2)	C3—C4	1.528 (4)
P2—O3	1.565 (2)	C3—C2	1.532 (4)
P2—Cl2	2.0047 (13)	C3—C1	1.533 (4)
P1—O5	1.446 (2)	C5—H5A	0.9900
P1—O1	1.555 (2)	C5—H5B	0.9900
P1—O2	1.571 (2)	C4—H4A	0.9900
P1—Cl1	2.0050 (14)	C4—H4B	0.9900
O4—C5	1.461 (3)	C1—H1A	0.9900
O2—C2	1.457 (4)	C1—H1B	0.9900
O3—C4	1.464 (4)	C2—H2A	0.9900

O1—C1	1.467 (4)	C2—H2B	0.9900
O6—P2—O4	114.00 (13)	O4—C5—H5A	109.4
O6—P2—O3	113.70 (14)	C3—C5—H5A	109.4
O4—P2—O3	106.12 (13)	O4—C5—H5B	109.4
O6—P2—C12	112.82 (11)	C3—C5—H5B	109.4
O4—P2—C12	104.61 (10)	H5A—C5—H5B	108.0
O3—P2—C12	104.71 (10)	O3—C4—C3	110.2 (3)
O5—P1—O1	113.75 (14)	O3—C4—H4A	109.6
O5—P1—O2	113.36 (14)	C3—C4—H4A	109.6
O1—P1—O2	106.39 (12)	O3—C4—H4B	109.6
O5—P1—C11	113.26 (12)	C3—C4—H4B	109.6
O1—P1—C11	104.73 (10)	H4A—C4—H4B	108.1
O2—P1—C11	104.49 (11)	O1—C1—C3	109.5 (2)
C5—O4—P2	119.3 (2)	O1—C1—H1A	109.8
C2—O2—P1	119.24 (19)	C3—C1—H1A	109.8
C4—O3—P2	119.6 (2)	O1—C1—H1B	109.8
C1—O1—P1	121.3 (2)	C3—C1—H1B	109.8
C5—C3—C4	109.2 (3)	H1A—C1—H1B	108.2
C5—C3—C2	112.5 (3)	O2—C2—C3	111.0 (3)
C4—C3—C2	108.6 (3)	O2—C2—H2A	109.4
C5—C3—C1	109.0 (3)	C3—C2—H2A	109.4
C4—C3—C1	108.0 (3)	O2—C2—H2B	109.4
C2—C3—C1	109.4 (3)	C3—C2—H2B	109.4
O4—C5—C3	111.2 (3)	H2A—C2—H2B	108.0

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1A \cdots O5 ⁱ	0.99	2.34	3.214 (4)	147
C1—H1B \cdots O6 ⁱⁱ	0.99	2.31	3.252 (4)	159
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