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cis- and *trans*-1,3-Diethoxy-1,3-diphosphorinane-1,3-dione

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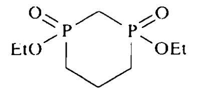
Abstract

The title compounds, *cis*- and *trans*-$C_8H_{18}O_4P_2$, crystallize with one and two independent molecules, respectively, in the asymmetric unit. These are the first structures of 1,3-diphosphorinanes with no further annelation. All three diphosphorinane rings are similar, with chair conformations that are flattened in the region of the P—C—P moiety. The ring angles at phosphorus are all less than, and those at carbon greater than, ideal tetrahedral angles [maximum of 116.21 (11)° for P—C—P in the *cis* isomer]. The acidic methylene groups, lying between the P atoms, are involved in the shortest C—H···O hydrogen bonds (H···O < 2.35 Å).

Comment

We are interested in the structures of diphosphorinane rings, both with and without further heteroatoms (Jones & Weinkauf, 1998, and references therein). We report here the structure of the *cis* and *trans* isomers of 1,3-diethoxy-1,3-diphosphorinane-1,3-dione, *cis*-(I) and *trans*-(I), respectively. A search of the Cambridge Structural Database (Version of October 1997; Allen & Kennard, 1993) indicated that these are the first structures involving a 1,3-diphosphorinane with no further annelation.



(I)

The *cis* or *trans* geometry was confirmed by the structure analyses (Figs. 1 and 2). The ethoxy substituents adopt the equatorial position in the *cis* isomer, but that

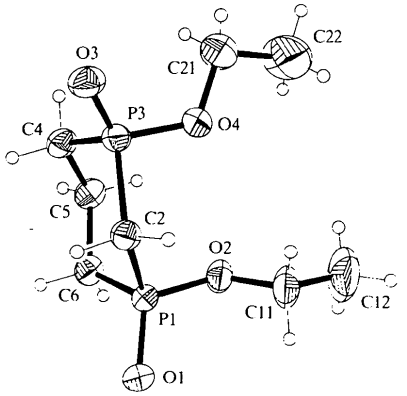


Fig. 1. The structure of the *cis* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

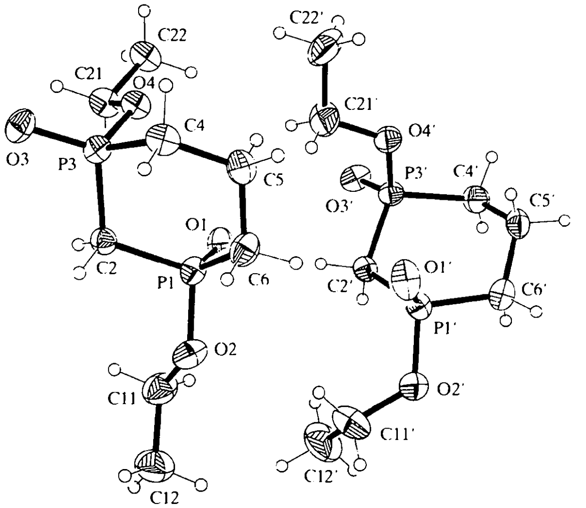


Fig. 2. The structure of both molecules of the *trans* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary. Only one position of the disordered ethoxy group is shown.

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at P1 in the *trans* isomer is forced to adopt the unfavourable axial position.

The two independent molecules of the *trans* isomer are, as expected, similar; the maximum differences in ring bond lengths and angles are 0.005 Å for C5—C6 and 1.79° for P1—C2—P3. A least-squares fit of both molecules, considering all ring atoms plus all O atoms, gave a mean deviation of 0.076 Å. There are appreciable differences (6°) in torsion angles involving C2 as a central atom. Bond lengths and angles in the *cis* isomer are closely similar.

In both isomers, the rings adopt a chair conformation, with absolute torsion angles between 41.82 (14) and 66.9 (2)°, and mean values of 53.1 (*cis*), and 55.9 and 53.6° (*trans*). The regions around C2 are flatter, with torsion angles about P1—C2 and P3—C2 (all < 50°) lower than those about C4—C5 and C5—C6 (all > 62°).

Ring bond angles are slightly lower than tetrahedral at P (105–107°) but appreciably wider at the C atoms (113–117°), especially at C2; such wide angles are common for P—C—P systems and can indeed be as high as 120°, as commented on in our earlier paper (Jones & Weinkauf, 1998).

The geometry of several C—H···O contacts suggests their classification as hydrogen bonds (Tables 2 and 4 show values with H···O < 2.6 Å, excluding disordered atoms). Particularly short H···O contacts (≤ 2.35 Å) are observed for the donor system C2—H; this methylene group, lying between the two P atoms, is the most acidic group. Similar effects were observed in our previous paper (Jones & Weinkauf, 1998).

Experimental

The title compounds were obtained from 1,3-dibromopropane and methanebis(phosphonous acid diethyl ester) and the isomers were separated chromatographically; details are given by Sebastian (1992). Single crystals were obtained by slow cooling of saturated solutions in dichloromethane/petroleum ether (303–313 K).

cis-(I) isomer

Crystal data

$C_8H_{18}O_4P_2$
$M_r = 240.16$
Monoclinic
$P2_1/n$
$a = 7.313$ (2) Å
$b = 9.028$ (2) Å
$c = 18.610$ (5) Å
$\beta = 97.34$ (2)°
$V = 1218.6$ (5) Å^3
$Z = 4$
$D_x = 1.309$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 46 reflections
$\theta = 10.0$–12.5°
$\mu = 0.346$ mm^{-1}
$T = 178$ (2) K
Tablet
0.7 × 0.5 × 0.1 mm
Colourless

Data collection

Nicolet $R3$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
5818 measured reflections
2794 independent reflections
2155 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

$\theta_{max} = 27.51$°
$h = -9 \rightarrow 0$
$k = -11 \rightarrow 11$
$l = -23 \rightarrow 24$
3 standard reflections every 147 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.121$
$S = 1.032$
2794 reflections
129 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.9590P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.469$ e Å^{-3}
$\Delta\rho_{min} = -0.398$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for cis-(I)*

P1—C2	1.803 (2)	C4—C5	1.538 (3)
C2—P3	1.793 (2)	C5—C6	1.538 (3)
P3—C4	1.799 (2)	P1—C6	1.794 (2)
C6—P1—C2	106.25 (10)	C5—C4—P3	114.40 (15)
P3—C2—P1	116.21 (11)	C4—C5—C6	113.63 (18)
C2—P3—C4	105.32 (10)	C5—C6—P1	115.50 (16)
C6—P1—C2—P3	−43.20 (15)	P3—C4—C5—C6	64.9 (2)
P1—C2—P3—C4	45.11 (15)	C4—C5—C6—P1	−62.5 (2)
C2—P3—C4—C5	−53.74 (18)	C2—P1—C6—C5	49.20 (18)

Table 2. *Hydrogen-bonding geometry (Å, °) for cis-(I)*

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O1^{i}	0.99	2.49	3.257 (3)	134.2
C6—H6B···O1^{i}	0.99	2.52	3.306 (3)	136.3
C2—H2B···O3^{ii}	0.99	2.31	3.282 (3)	166.9
C4—H4B···O3^{iii}	0.99	2.56	3.463 (3)	151.9
C21—H21B···O3^{iii}	0.99	2.49	3.327 (4)	141.6

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

trans-(I) isomer

Crystal data

$C_8H_{18}O_4P_2$
$M_r = 240.16$
Monoclinic
$P2_1/n$
$a = 7.431$ (2) Å
$b = 18.715$ (5) Å
$c = 17.183$ (6) Å
$\beta = 99.06$ (3)°
$V = 2359.8$ (12) Å^3
$Z = 8$
$D_x = 1.352$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0$–11.5°
$\mu = 0.357$ mm^{-1}
$T = 178$ (2) K
Prism
0.7 × 0.5 × 0.5 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
11 525 measured reflections
5451 independent reflections
4144 reflections with
$I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.56°$
$h = -9 \rightarrow 0$
$k = -24 \rightarrow 24$
$l = -22 \rightarrow 22$
3 standard reflections
every 147 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.105$
$S = 1.053$
5451 reflections
270 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 1.381P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.35$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for trans-(I)*

P1—C2	1.799 (2)	P1′—C2′	1.802 (2)
P3—C2	1.798 (2)	P3′—C2′	1.801 (2)
P3—C4	1.793 (2)	P3′—C4′	1.794 (2)
C4—C5	1.536 (3)	C4′—C5′	1.536 (3)
C5—C6	1.535 (3)	C5′—C6′	1.530 (3)
P1—C6	1.792 (2)	P1′—C6′	1.794 (2)
C6—P1—C2	105.64 (10)	C6′—P1′—C2′	106.13 (10)
P3—C2—P1	113.72 (10)	P3′—C2′—P1′	115.51 (11)
C4—P3—C2	105.55 (10)	C4′—P3′—C2′	106.61 (10)
C5—C4—P3	114.53 (14)	C5′—C4′—P3′	115.02 (14)
C6—C5—C4	113.50 (17)	C6′—C5′—C4′	113.19 (17)
C5—C6—P1	113.09 (15)	C5′—C6′—P1′	113.34 (15)
C6—P1—C2—P3	49.24 (13)	C6′—P1′—C2′—P3′	−44.09 (14)
C4—P3—C2—P1	−47.69 (13)	C4′—P3′—C2′—P1′	41.82 (14)
C2—P3—C4—C5	52.99 (16)	C2′—P3′—C4′—C5′	−49.61 (18)
P3—C4—C5—C6	−64.2 (2)	P3′—C4′—C5′—C6′	64.6 (2)
C4—C5—C6—P1	65.3 (2)	C4′—C5′—C6′—P1′	−66.9 (2)
C2—P1—C6—C5	−55.69 (17)	C2′—P1′—C6′—C5′	54.31 (17)

Table 4. *Hydrogen-bonding geometry (Å, °) for trans-(I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2′—H2′2···O1	0.99	2.35	3.327 (3)	169.6
C2′—H2′1···O3^{i}	0.99	2.44	3.214 (2)	134.3
C4′—H4′1···O3^{i}	0.99	2.56	3.336 (3)	134.9
C2—H2*A*···O1′^{ii}	0.99	2.28	3.236 (2)	163.3
C6—H6*B*···O1′	0.99	2.54	3.476 (3)	158.1
C21—H21*B*···O1′^{ii}	0.99	2.52	3.434 (3)	153.8
C2—H2*B*···O3′^{iii}	0.99	2.45	3.284 (3)	141.5

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

H atoms were included using rigid methyl groups (starting positions taken from difference syntheses and then allowed to rotate but not tip) or a riding model starting from calculated positions. For the *trans* isomer, the ethoxy group O2—C11—C12 of molecule 2 is disordered over two positions, with occupancy factors of 0.748 (6) and 0.252 (6). The minor component is omitted from the discussion. An appropriate system of restraints was used to stabilize the refinement; details are given in the final instruction file, which is included in the deposited material. The relatively high *U* values of some terminal methyl groups (~0.1 Å^2) lead to librational shortening of some ethyl C—C bonds.

For both compounds, data collection: *P*3 *Software* (Nicolet Instrument Corporation, 1987); cell refinement: *P*3 *Software*; data reduction: *XDISK* in *P*3 *Software*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*93.

The compounds were synthesized and entrusted to us by Dr M. Sebastian and Professor M. Fild, to whom we are grateful. We thank the Fonds der Chemischen Industrie for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1249). Services for accessing these data are described at the back of the journal.

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cis- and *trans*-3,5-Diethoxy-1-oxa-3,5-diphosphorinane-3,5-dione

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Abstract

The title compounds, *cis*- and *trans*-$C_7H_{16}O_5P_2$, display chair conformations of the heterocyclic rings, with much larger absolute torsion angles around C—O—C (> 72°) than around P—C—P (< 47°). Ring angles are lower than tetrahedral at phosphorus, but higher at carbon and oxygen, with a maximum of 116.03 (12)° for the P—C—P angle of the *cis* isomer. Several C—H···O contacts, including one as short as H···O = 2.27 Å, can be classified as hydrogen bonds.

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