Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
11 525 measured reflections
5451 independent reflections
4144 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.033$

$\theta_{\max} = 27.56°$
$h = -9 \rightarrow 0$
$k = -24 \rightarrow 24$
$l = -22 \rightarrow 22$
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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ 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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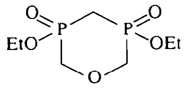
Comment

We are interested in the structures of diphosphorinane rings, both with and without further heteroatoms (Jones & Fischer, 1998, and references therein). We report here the structure of the *cis* and *trans* isomers of 3,5-diethoxy-1-oxa-3,5-diphosphorinane-3,5-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-oxa-3,5-diphosphorinane with no further annelation.



(I)

The *cis* or *trans* geometry was confirmed by the structure analyses (Figs. 1 and 2). The compounds are not isostructural with the analogues having CH_2 instead of O in the ring (Jones & Fischer, 1998). The ethoxy substituents adopt equatorial positions in the *cis* isomer, but in the *trans* isomer, that at P5 is forced to adopt the unfavourable axial position.

Ring bond lengths in both isomers are essentially identical. The rings adopt chair conformations, with absolute torsion angles between 38.15 (16) and 74.5 (2)°, mean value 54.7°, for the *cis* isomer, and between 43.00 (14) and 76.02 (19)°, mean value 58.2°, for the *trans* isomer. The regions around C4 (between the P atoms) are flatter, with torsion angles about P3—C4 and P5—C4 (*cis*: < 39°; *trans*: < 47°) much lower than those around O1—C2 and O1—C6 (*cis*: > 73°; *trans*: > 72°). It is noteworthy that the *cis* isomer is much flatter in the C4 region than the *trans* isomer; the situation for the CH_2 analogue (Jones & Fischer, 1998) was not clear-cut, with the two independent molecules of the *trans* isomer differing as much from each other as from the *cis* isomer.

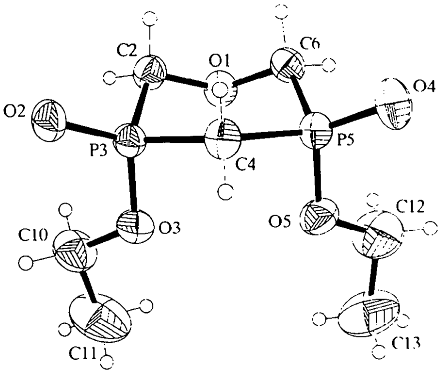


Fig. 1. The structure of the *cis* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

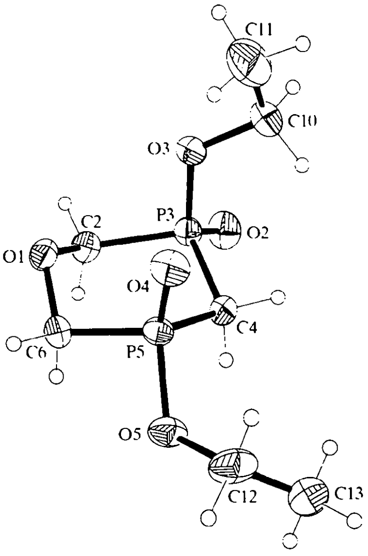


Fig. 2. The structure of the *trans* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

Ring bond angles have slightly lower than ideal tetrahedral values at P (104–106°), but have wider values at the C and O atoms (110–116°), with the largest value of 116.03 (12)° occurring at C4 in the *cis* isomer. Wide angles (up to 120°) are common in P—C—P systems, as commented on in our earlier paper (Jones & Weinkauf, 1998). Several contacts of the type C—H···O can be classified as hydrogen bonds (see Tables 2 and 4). Particularly short are those contacts involving C4 of the *trans* isomer (H···O = 2.27 and 2.28 Å).

Experimental

The title compounds were obtained from 1,3-dibromo-2-oxapropane and methanebis(phosphonous acid diethyl ester) in refluxing xylene; isomers were separated chromatographically [details are given by Sebastian (1992)]. Single crystals were obtained by gas phase diffusion of diethyl ether into a dichloromethane solution (*cis*) or by slow cooling of a saturated solution in dichloromethane/diethyl ether (*trans*).

cis-(I) isomer

Crystal data

$C_7H_{16}O_5P_2$
$M_r = 242.14$
Monoclinic
$C2/c$
$a = 25.108 (10)$ Å
$b = 10.954 (5)$ Å
$c = 8.547 (4)$ Å
$\beta = 94.82 (4)°$
$V = 2342.6 (18)$ Å^3
$Z = 8$
$D_x = 1.373$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0–12.5°$
$\mu = 0.366$ mm^{-1}
$T = 293 (2)$ K
Tablet
0.70 × 0.50 × 0.15 mm
Colourless

Data collection

Nicolet $R3$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3361 measured reflections
2078 independent reflections
1719 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$

$\theta_{\rm max} = 25.05°$
$h = -29 \rightarrow 29$
$k = 0 \rightarrow 13$
$l = -10 \rightarrow 4$
3 standard reflections every 147 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.105$
$S = 1.031$
2078 reflections
129 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0570P)^2 + 1.8624P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C2	1.431 (3)	P5—C4	1.794 (2)
P3—C2	1.812 (2)	P5—C6	1.810 (2)
P3—C4	1.797 (2)	O1—C6	1.422 (3)
C6—O1—C2	113.86 (17)	P5—C4—P3	116.03 (12)
O1—C2—P3	112.31 (15)	C4—P5—C6	104.91 (11)
C4—P3—C2	105.22 (10)	O1—C6—P5	112.50 (15)
C6—O1—C2—P3	−73.7 (2)	C6—P5—C4—P3	38.40 (16)
C4—P3—C2—O1	51.20 (18)	C4—P5—C6—O1	−52.28 (18)
C2—P3—C4—P5	−38.15 (16)	C2—O1—C6—P5	74.5 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*A*···O1$^{\rm i}$	0.97	2.50	3.379 (4)	150.2
C10—H10*B*···O2$^{\rm ii}$	0.97	2.51	3.457 (4)	166.7
C6—H6*B*···O4$^{\rm iii}$	0.97	2.42	3.380 (3)	171.7

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

***trans*-(I) isomer**

Crystal data

$C_7H_{16}O_5P_2$
$M_r = 242.14$
Orthorhombic
$Pna2_1$
$a = 9.058$ (2) Å
$b = 15.312$ (3) Å
$c = 8.270$ (2) Å
$V = 1147.0$ (4) Å^3
$Z = 4$
$D_x = 1.402$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 48 reflections
$\theta = 10.0$–$11.5°$
$\mu = 0.374$ mm^{-1}
$T = 178$ (2) K
Block
0.5 × 0.4 × 0.4 mm
Colourless

Data collection

Nicolet $R3$ diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2633 measured reflections
2633 independent reflections
2368 reflections with $I > 2\sigma(I)$

$\theta_{\rm max} = 27.50°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 19$
$l = -10 \rightarrow 10$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.080$
$S = 1.027$
2633 reflections
129 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0516P)^2 + 0.0822P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (10)

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

O1—C2	1.434 (2)	P5—C4	1.805 (2)
P3—C2	1.814 (2)	P5—C6	1.809 (2)
P3—C4	1.804 (2)	O1—C6	1.432 (3)
C6—O1—C2	113.49 (16)	P3—C4—P5	112.70 (11)
O1—C2—P3	113.00 (13)	C4—P5—C6	104.25 (9)
C4—P3—C2	105.12 (9)	O1—C6—P5	110.00 (13)
C6—O1—C2—P3	−72.14 (19)	C6—P5—C4—P3	46.78 (13)
C4—P3—C2—O1	51.71 (18)	C4—P5—C6—O1	−59.64 (17)
C2—P3—C4—P5	−43.00 (14)	C2—O1—C6—P5	76.02 (19)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4*B*···O1$^{\rm i}$	0.99	2.28	3.145 (3)	144.8
C4—H4*A*···O2$^{\rm ii}$	0.99	2.27	3.237 (2)	163.8
C6—H6*A*···O3$^{\rm i}$	0.99	2.56	3.467 (3)	151.6
C10—H10*A*···O4$^{\rm iii}$	0.99	2.48	3.455 (3)	168.5
C12—H12*A*···O4$^{\rm iv}$	0.99	2.42	3.318 (3)	151.3

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

Methyl H atoms were included using rigid methyl groups. Starting positions were taken from difference syntheses and then allowed to rotate but not to tip. Methylene H atoms were subjected to a riding model starting from calculated positions. For the *cis* isomer, the shortened C—C bonds in the side chains probably reflect libration effects. For the *trans* isomer, the absolute structure was determined by the method of Flack (1983) using 1349 Friedel pairs, and the origin was fixed according to the method of Flack & Schwarzenbach (1988).

For both compounds, data collection: *P3 Software* (Nicolet Instrument Corporation, 1987); cell refinement: *P3 Software*; data reduction: *XDISK* in *P3 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL93*.

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: BM1250). Services for accessing these data are described at the back of the journal.

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X-ray Structure Investigations of Potential β-Blockers. III

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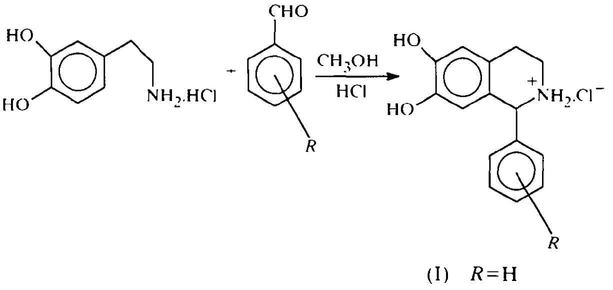
Abstract

X-ray studies of 6,7-dihydroxy-1-phenyl-1,2,3,4-tetrahydroisoquinolinium chloride hydrate ($C_{15}H_{16}NO_2^+.Cl^-.H_2O$), 6,7-dihydroxy-1-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolinium chloride ($C_{16}H_{18}NO_3^+.Cl^-$) and 6,7-dihydroxy-1-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinolinium chloride ($C_{15}H_{15}N_2O_4^+.Cl^-$) show that the saturated parts of the rings have deformed half-chair conformations, with equatorially attached phenyl rings. All three structures are ionic, and hydrogen bonds are observed.

Comment

This paper is a continuation of the structural work on saturated isoquinoline derivatives reported by Olszak (Olszak *et al.*, 1994, 1996). Tetrahydroisoquinolines are known to exhibit β-adrenomimetic activity (Brzezińska, 1994). A group of 1-aryl-6,7-dihydroxy-1,2,3,4-tetrahydroisoquinoline [where 1-aryl is phenyl in (I), 2-methoxyphenyl in (II) and 4-nitrophenyl in (III)] derivatives was synthesized at the Institute of Chemistry and Technology of Drugs, University of Medicine, Łódź, in order to determine the role of the hydrophobic group at C1 on the activity of these structures as β-adrenoreceptors (Brzezińska *et al.*, 1996).



(I) R=H
(II) R=2-OCH$_3$
(III) R=Δ-NO$_2$

The title structures, (I).H_2O, (II) and (III), are shown in perspective views with the atomic numbering schemes in Figs. 1–3. Selected bond lengths, bond angles and details of the hydrogen-bonding geometry are listed in Tables 1–6.

The title structures differ slightly from each other in the substituents on the phenyl group (see Scheme). The saturated parts of the molecules have either half-chair, (I), or deformed half-chair tending towards twisted-boat conformations, (II) and (III). The Cremer & Pople (1975) puckering parameters for the N1–C1–C9–C8–C3–C2 atom sequence are: Q = 0.504 (2), 0.498 (3), 0.563 (2) Å; φ_2 = 165.2 (4), 142.4 (4), 156.4 (3)°; θ_2 = 131.3 (3), 129.1 (3), 128.9 (2)° for (I), (II) and (III), respectively. There are pseudo-twofold axes passing through the midpoints of the N1—C2 and C8—C9 bonds [asymmetry parameters (Nardelli, 1983*a*): Δ_2 =

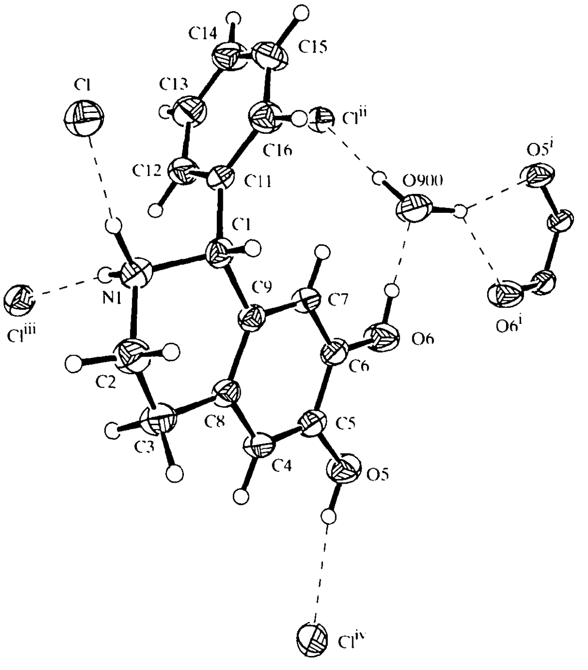


Fig. 1. Plot of (I), showing the atomic numbering scheme. Displacement ellipsoids are shown at 40% probability. Symmetry codes are as given in Table 2.

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