Acta Cryst. (1998). C**54**, 1449–1451

trans-1,3-Diethoxy-5,5-dimethyl-1,3-diphospha-5-silacyclohexane-1,3-dione

Peter G. Jones* and Andreas Weinkauf

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

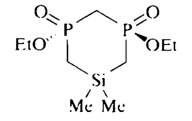
(Received 12 March 1998; accepted 1 May 1998)

Abstract

The title compound, $C_9H_{22}O_4P_2Si$, is the first 1,3-diphospha-5-silacyclohexane for which an X-ray structure has been reported. It crystallizes with two independent molecules, which are closely similar. The rings adopt a chair conformation with mean absolute torsion angles of 55.67 and 55.21°. Ring bond angles at carbon are wider than ideal tetrahedral, with values in the range 114.09 (11)–118.05 (11)°. There are several C—H···O hydrogen bonds, of which the shortest by far is C2—H2*A*···O2′, with H···O = 2.25 Å and C···O = 3.236 (3) Å.

Comment

We are interested in the structures of diphosphorinane rings containing further heteroatoms (Jones & Weinkauf, 1994, 1997). We report here the structure of *trans*-1,3-diethoxy-5,5-dimethyl-1,3-diphospha-5-silacyclohexane-1,3-dione, (I). A search of the Cambridge Structural Database (Version of October 1997; Allen & Kennard, 1993) indicated that this is the first structure involving a 1,3-diphospha-5-silacyclohexane ring.



(I)

The *trans* geometry was confirmed by the structure analysis (Fig. 1). The ethoxy substituent at P1 adopts the unfavourable axial position. The two independent molecules are closely similar; the maximum differences in ring bond lengths and angles are 0.013 Å for P1—C2 and 1.08° for P1—C6—Si5. A least-squares fit of both molecules, considering all ring atoms plus all O atoms, gave a mean deviation of only 0.03 Å. The ethoxy groups all display extended conformations.

The rings adopt a chair conformation, with absolute torsion angles between 48.89 (14) and 62.61 (14)°, and mean values of 55.67 and 55.21°, for the two molecules, respectively. A 1,4,2,6-oxathiadiphosphorinane, in contrast, showed much flatter rings, with a C—P—O—P torsion angle as low as 27.71 (14)° (Jones & Weinkauf, 1997).

Ring bond angles are approximately tetrahedral at P and Si, but widen to 117.47 (11) and 116.71 (11)° at C2,

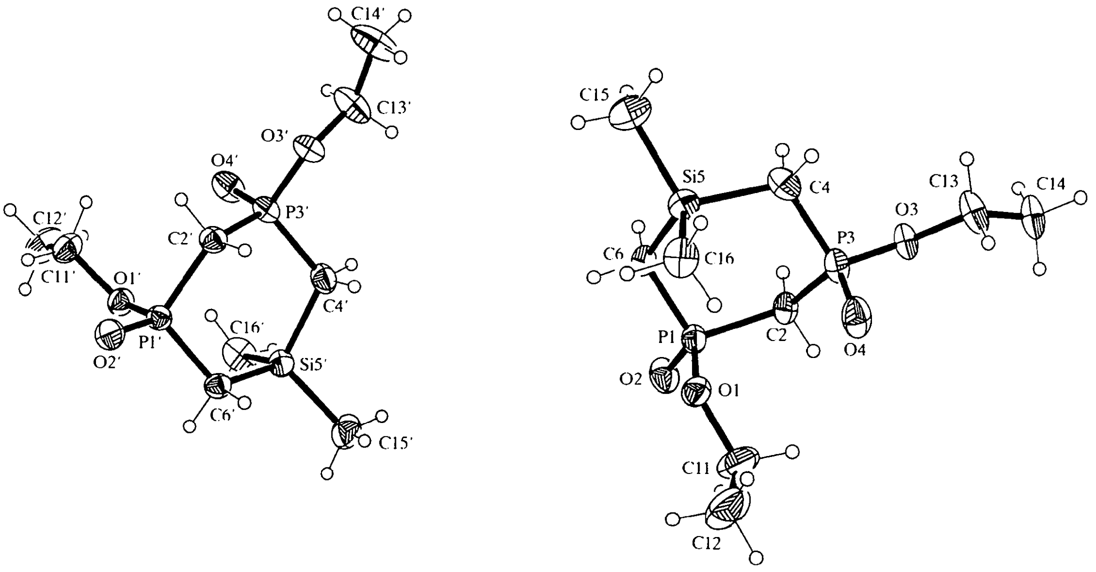


Fig. 1. The structures of both molecules of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary. Only one position of the disordered ethoxy group is shown.

to 114.09 (11) and 114.66 (11)° at C4, and to 116.97 (10) and 118.05 (11)° at C6. Such wide angles are common for P—C—P systems, *e.g.* 119.6–120.4 (2)° in the four independent molecules of 3,5-diisopropoxy-3,5-dioxo-1,3,5-thiadiphosphorinane (two in the *cis* and two in the *trans* structure; Jones & Weinkauf, 1994).

An analysis of non-bonded contacts reveals several interactions that could be classified as C—H···O hydrogen bonds (Table 2 includes those with H···O < 2.6 Å). The interaction C2—H2*A*···O2′(*x*, *y*, *z* − 1), with H···O = 2.25 Å and C···O = 3.236 (3) Å, is strikingly short.

Experimental

The title compound was obtained from 1,3-diiodo-2-silapropane and methanebis(phosphonous acid diethyl ester); details are given by Sebastian (1992). Single crystals were obtained by slow cooling of a saturated solution in petroleum ether (303–313 K).

Crystal data

$C_9H_{22}O_4P_2Si$
$M_r = 284.30$
Triclinic
$P\bar{1}$
$a = 11.017 (3)$ Å
$b = 11.511 (3)$ Å
$c = 14.292 (3)$ Å
$\alpha = 100.61 (2)°$
$\beta = 103.52 (2)°$
$\gamma = 117.69 (2)°$
$V = 1467.4 (6)$ Å^3
$Z = 4$
$D_x = 1.287$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0–11.5°$
$\mu = 0.375$ mm^{-1}
$T = 178 (2)$ K
Prism
0.7 × 0.5 × 0.3 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
6266 measured reflections
5147 independent reflections
4481 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$

$\theta_{\rm max} = 25°$
$h = -13 \rightarrow 12$
$k = -12 \rightarrow 13$
$l = -16 \rightarrow 16$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.044$
5147 reflections
310 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 1.0860P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.035$
$\Delta\rho_{\rm max} = 0.360$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.436$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P1—C2	1.803 (2)	P1′—C2′	1.816 (2)
C2—P3	1.795 (2)	C2′—P3′	1.802 (2)
P3—C4	1.788 (2)	P3′—C4′	1.787 (2)
C4—Si5	1.893 (2)	C4′—Si5′	1.899 (2)
Si5—C6	1.885 (2)	Si5′—C6′	1.884 (2)
P1—C6	1.779 (2)	P1′—C6′	1.774 (2)
C6—P1—C2	106.86 (10)	C6′—P1′—C2′	106.28 (9)
P3—C2—P1	117.47 (11)	P3′—C2′—P1′	116.71 (11)
C4—P3—C2	105.86 (10)	C4′—P3′—C2′	105.47 (10)
P3—C4—Si5	114.09 (11)	P3′—C4′—Si5′	114.66 (11)
C6—Si5—C4	105.67 (9)	C6′—Si5′—C4′	106.39 (9)
P1—C6—Si5	116.97 (10)	P1′—C6′—Si5′	118.05 (11)
C6—P1—C2—P3	56.65 (14)	C6′—P1′—C2′—P3′	58.39 (14)
P1—C2—P3—C4	−60.55 (14)	P1′—C2′—P3′—C4′	−62.61 (14)
C2—P3—C4—Si5	58.68 (14)	C2′—P3′—C4′—Si5′	58.28 (14)
P3—C4—Si5—C6	−54.77 (14)	P3′—C4′—Si5′—C6′	−52.02 (15)
C4—Si5—C6—P1	51.63 (14)	C4′—Si5′—C6′—P1′	48.89 (14)
C2—P1—C6—Si5	−51.73 (14)	C2′—P1′—C6′—Si5′	−51.04 (13)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6*A*···O1$^{\rm i}$	0.99	2.51	3.493 (3)	170.1
C11′—H11*D*···O2$^{\rm ii}$	0.99	2.58	3.551 (3)	166.1
C13′—H13*C*···O2$^{\rm iii}$	0.99	2.41	3.357 (3)	160.2
C15′—H15*D*···O2$^{\rm iv}$	0.98	2.52	3.423 (3)	153.8
C16—H16*C*···O2$^{\rm i}$	0.98	2.53	3.509 (3)	175.6
C6′—H6′2···O4$^{\rm i}$	0.99	2.43	3.309 (3)	148.0
C6′—H6′1···O1′$^{\rm v}$	0.99	2.58	3.565 (2)	174.0
C2—H2*A*···O2′$^{\rm vi}$	0.99	2.25	3.236 (3)	170.7
C16′—H16*F*···O2′$^{\rm v}$	0.98	2.59	3.572 (3)	176.7
C2—H2*B*···O4′$^{\rm iii}$	0.99	2.56	3.410 (3)	144.0

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

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. The ethoxy group O3—C13—C14 of molecule 1 is disordered over two positions, with occupancy factors of 0.803 (9) and 0.197 (9). The atoms of the minor component were refined with isotropic displacement parameters, and mention of this 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.

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 structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The compound was 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: BM1247). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Jones, P. G. & Weinkauf, A. (1994). *Z. Kristallogr.* **209**, 177–179.
Jones, P. G. & Weinkauf, A. (1997). *Acta Cryst.* C**53**, 615–616.
Nicolet Instrument Corporation (1987). *P3 Software*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.
Sebastian, M. (1992). PhD thesis, Technical University of Braunschweig, Germany.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994). *XP. Interactive Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1451–1453

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

Peter G. Jones* and Axel K. Fischer†

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

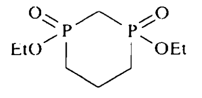
(*Received 13 March 1998; accepted 1 May 1998*)

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

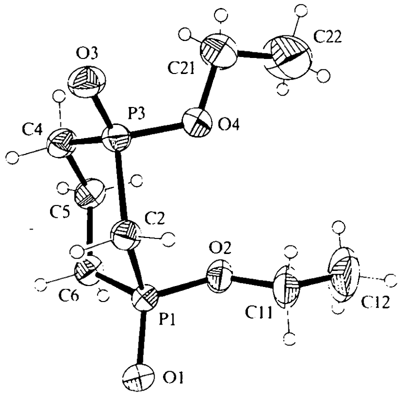


Fig. 1. The structure of the *cis* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

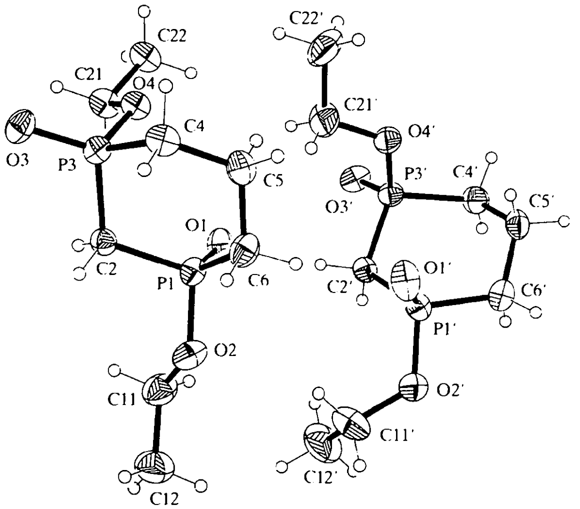


Fig. 2. The structure of both molecules of the *trans* isomer in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary. Only one position of the disordered ethoxy group is shown.

---

† Current address: Chemisches Institut, Universität Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998