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# *trans*-3,5-Diphenyl-1,4,2,6-oxathiadiphosphorinane-3,5-dione

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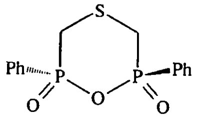
## Abstract

The title compound, $C_{14}H_{14}O_3P_2S$, exhibits a flattened chair conformation of the heterocycle. The ring bond angle at oxygen is extremely wide at 137.12 (9)°, whereas that at sulfur is narrow at 98.78 (9)°.

## Comment

The title compound, (I), was synthesized as part of a study of the oxidations of various diphosphanes and diphospholanes (Sebastian, 1992). As far as we are aware, no structures of the ring system 1,4,2,6-oxathiadiphosphorinane have been published [Cambridge Structural Database (version of April 1996); Allen & Kennard, 1993]. The X-ray structure determination revealed the *trans* disposition of the phenyl substituents [torsion angles O2—P3···P5—O3 −140.0 (1) and C7—P3···P5—C13 129.9 (1)°].



(I)

The heterocycle adopts a distorted chair conformation; the absolute torsion angles in the flatter region C2—P3—O4—P5 lie in the range 28–40°, while the others are in the range 58–74° (Table 1). If the atoms C2, P3, P5 and C6 are regarded as defining a ring plane (mean deviation 0.08 Å), then the S1 and O4 atoms lie 1.017 (2) and 0.301 (1) Å, respectively, on opposite sides of this plane.

The ring angle P3—O4—P5 is extremely wide at 137.12 (9)° [P3···P5 3.001 (2) Å], whereas C2—S1—C6 is narrow at 98.78 (9)°. A similarly wide P—O—P angle of 135.2 (1)° was observed in the P—O—P—C—O—C ring of *cis*-2,4-dimethyl-1,5-diphenyl-3,9-dioxa-2,4-diphosphabicyclo[3.3.1]nonane-2,4-dione, whereas the corresponding angle in the *trans* isomer was narrower [128.4 (1)°; Rudi, Reichman, Goldberg & Kashman, 1983]. C—S—C angles of 100.47, 101.01 (14) and 102.2, 101.6 (2)° were observed in the P—C—P—C—S—C rings of two independent molecules of *trans*- and *cis*-3,5-diisopropoxy-3,5-dioxo-1,3,5-thiadiphosphorinane (Jones & Weinkauf, 1994).

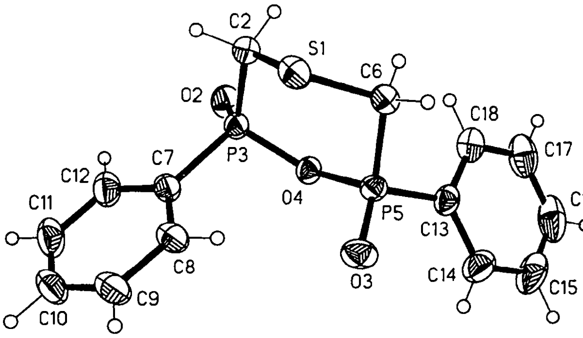


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary.

## Experimental

The title compound was obtained by air oxidation of 3,4-diphenyl-1,3,4-thiadiphospholane and recrystallized from dichloromethane–petroleum ether (30/40) solution (Sebastian, 1992).

*Crystal data*

$C_{14}H_{14}O_3P_2S$
$M_r = 324.25$
Triclinic
$P\overline{1}$
$a = 9.142 (4)$ Å
$b = 9.687 (4)$ Å
$c = 10.449 (5)$ Å
$\alpha = 113.07 (3)°$
$\beta = 94.14 (3)°$
$\gamma = 115.15 (3)°$
$V = 738.3 (6)$ Å$^3$
$Z = 2$
$D_x = 1.459$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10–12°$
$\mu = 0.439$ mm$^{-1}$
$T = 178 (2)$ K
Block
0.65 × 0.60 × 0.40 mm
Colourless

*Data collection*

Nicolet *R*3 diffractometer
$\omega$ scans
Absorption correction: none
2707 measured reflections
2587 independent reflections
2342 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.0089$

$\theta_{\max} = 25°$
$h = -10 \rightarrow 0$
$k = -10 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
every 147 reflections
intensity decay: none

*Refinement*

Refinement on $F^2$
$R(F) = 0.0301$
$wR(F^2) = 0.0811$
$S = 1.038$
2587 reflections
181 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.4395P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.381$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.340$ e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| S1—C2 | 1.811 (3) | P3—C7 | 1.792 (2) |
| S1—C6 | 1.812 (2) | O4—P5 | 1.619 (2) |
| C2—P3 | 1.808 (2) | P5—O3 | 1.472 (2) |
| P3—O2 | 1.471 (2) | P5—C13 | 1.786 (2) |
| P3—O4 | 1.6060 (14) | P5—C6 | 1.795 (2) |
| C2—S1—C6 | 98.78 (9) | P3—O4—P5 | 137.12 (9) |
| P3—C2—S1 | 114.71 (11) | O3—P5—O4 | 113.26 (9) |
| O2—P3—O4 | 110.78 (9) | O3—P5—C13 | 113.54 (9) |
| O2—P3—C7 | 112.18 (9) | O4—P5—C13 | 102.83 (9) |
| O4—P3—C7 | 105.28 (8) | O3—P5—C6 | 113.94 (9) |
| O2—P3—C2 | 112.58 (10) | O4—P5—C6 | 102.51 (9) |
| O4—P3—C2 | 105.26 (9) | C13—P5—C6 | 109.68 (9) |
| C7—P3—C2 | 110.28 (9) | P5—C6—S1 | 109.17 (10) |
| C6—S1—C2—P3 | 63.50 (12) | P3—O4—P5—C6 | −37.50 (14) |
| S1—C2—P3—O4 | −39.13 (12) | O4—P5—C6—S1 | 58.06 (11) |
| C2—P3—O4—P5 | 27.71 (14) | C2—S1—C6—P5 | −73.53 (11) |

Data collection: *P*3 *Software* (Nicolet, 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 crystals of (I) were kindly provided by Professor M. Fild and Dr M. Sebastian of this Institute. We thank the Fonds der Chemischen Industrie for financial support.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1232). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 3-Acetonylbicyclo[6.3.0]undecane-2,6-dione, (I), 7-Acetonyl-4,4-dimethylbicyclo[6.3.0]undecane-2,6-dione, (II), 7,12-Dihydroxy-12-methyltetracyclo[8.2.1.$0^{1,5}$.$0^{7,11}$]tridecan-13-one Monohydrate, (III), and 8,8-Dimethyltricyclo[9.3.0.$0^{2,6}$]tetradec-5-ene-4,10-dione, (IV)

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## Abstract

The crystal structures of the four title compounds, $C_{14}H_{20}O_3$, (I), $C_{16}H_{24}O_3$, (II), $C_{14}H_{20}O_3.H_2O$, (III), and $C_{16}H_{22}O_2$, (IV), which were obtained during studies of the preparation of $C_5$–$C_8$–$C_5$ fused-ring compounds, have been determined by X-ray diffraction.

## Comment

The synthesis of $C_5$–$C_8$–$C_5$ fused-ring compounds by intramolecular aldol reaction has been investigated (Umehara *et al.*, 1993; Kawata *et al.*, 1993). Although a $C_5$–$C_6$–$C_5$–$C_5$ tetracyclic compound, (III), was obtained from (I), the desired $C_5$–$C_8$–$C_5$ fused-ring compound (IV) was yielded from (II). Epimerization of (II) seems to occur under basic conditions. A strain-energy calculation by *MM*2 (Allinger, 1977) indicates that structure (IV) is more stable than the epimer by 21.8 kJ mol$^{-1}$. The eight-membered ring adopts a boat–chair form in compounds (I) and (IV), and a chair–chair form in compound (II). The crystal of (III) was obtained as the monohydrate and there are intermolecular O—H···O hydrogen bonds (see Table 4). The six-membered ring of compound (III) has a flattened boat form and the O17