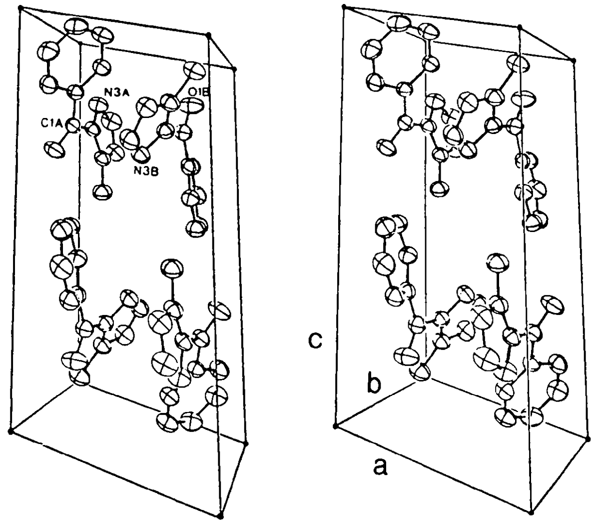

Fig. 2. Stereoscopic view of the unit cell showing the molecular packing. Thermal ellipsoids for non-hydrogen atoms represent 50% probability.

N(3) of the two adjacent molecules. Because of the size of (V), either C(1) or O(1) may be closest to N(3) and the distance variation is as predicted for the interaction of an electron-rich atom with a strong C=O dipole. When C(1) is closest to N(3), the distance is 3·34 Å [C(1)*A* to N(3)*B*]; when O(1) is closest to N(3), the distance is 4·05 Å [O(1)*B* to N(3)*A*].

We thank the National Institutes of Health and McNeil Laboratories for grants supporting part of this work, M. Y. Bernheim for her contributions in solving the structure, and J. P. Pepe for early experimental work on the fragmentation.

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The Structure of 2-Oxo-2′-thioxobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) Sulphide*

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(*Received* 9 *July* 1980; *accepted* 17 *October* 1980)

Abstract. $C_{10}H_{20}O_5P_2S_2$, M_r = 346·3, $F(000)$ = 728, orthorhombic, $P2_12_12_1$, a = 13·681 (2), b = 11·144 (2), c = 10·579 (2) Å, V = 1612·9 Å^3, Z = 4, D_m = 1·42 (1), D_c = 1·430 Mg m^{-3}, Cu $K\alpha$ radiation, λ = 1·5418 Å, μ = 4·8 mm^{-1}. The structure was solved by direct methods and refined to R = 0·045 for 1142 independent reflections. The symmetry of the bicyclic molecules is approximately 2. The two structurally independent dioxaphosphorinane rings have a partially flattened chair conformation with the P=O and P=S bonds in the equatorial positions. Unusual lengths for these bonds have been observed: P—O(12) = 1·538 (7) Å is longer and P—S(2) = 1·874 (3) Å is shorter than in other similar phosphates.

Introduction. The crystal and molecular structure determination of the title compound is part of an investigation of six-membered bicyclic organic pyro- and thiopyrophosphates. Structures and conformations of substituted 1,3,2-dioxaphosphorinanes have been of interest in recent years. The rings display

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* Alternative name: 2-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-ylthio)-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide.

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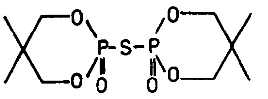
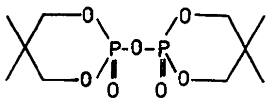
a flexible chair conformation, which can be influenced by substituents to give a wide range of degrees of flattening.

The P=O or P=S bonds can be equatorially or axially sited with respect to the central plane of the ring, which gives the possibility of the formation of geometrical isomers (Wieczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk & Ziemnicka, 1979). We have already reported the X-ray structure analyses of the compounds (I), (II) and (III) (Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Bukowska-Strzyżewska & Dobrowolska, 1978, 1980).


(I)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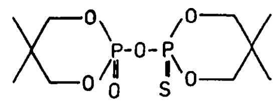
(III)

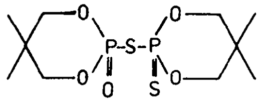
(IV)

Table 1. *Positional* ($\times 10^4$) *and isotropic thermal parameters for* 2-*oxo*-2′-*thioxobis*(5,5-*dimethyl*-1,3,2-*dioxaphosphorinanyl*) *sulphide with e.s.d.'s in parentheses*

$$B_{eq} = (B_{11}B_{22}B_{33})^{1/3}.$$

	x	y	z	B_{eq} (Å^2)
S(4)	1408 (2)	4722 (2)	2312 (2)	4·8 (1)
P(2)	2365 (2)	3698 (2)	3439 (2)	4·2 (1)
S(2)	1798 (2)	2873 (2)	4798 (2)	6·5 (1)
O(1)	2956 (4)	2843 (4)	2529 (5)	4·7 (3)
O(3)	3104 (4)	4714 (4)	3853 (4)	4·4 (3)
C(4)	3797 (6)	5197 (6)	2937 (7)	4·5 (4)
C(5)	4361 (6)	4206 (6)	2267 (7)	4·7 (4)
C(6)	3631 (7)	3371 (7)	1626 (8)	5·6 (5)
C(7)	4994 (6)	3507 (7)	3223 (7)	5·6 (5)
C(8)	4999 (7)	4791 (9)	1269 (8)	6·8 (6)
P(12)	523 (2)	3419 (2)	1451 (3)	4·8 (1)
O(11)	−62 (5)	2760 (5)	2514 (7)	4·8 (4)
O(12)	1056 (5)	2568 (6)	539 (6)	5·7 (4)
O(13)	−251 (5)	4247 (7)	769 (7)	5·6 (5)
C(14)	−972 (8)	4877 (10)	1518 (11)	5·1 (7)
C(15)	−1517 (8)	4065 (9)	2406 (10)	4·5 (6)
C(16)	−783 (8)	3415 (9)	3256 (9)	5·2 (6)
C(17)	−2137 (7)	3130 (9)	1689 (10)	7·0 (7)
C(18)	−2183 (8)	4836 (11)	3257 (12)	5·9 (8)

In this paper we present the structure of 2-oxo-2′-thioxobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) sulphide (IV). Colourless crystals were obtained from a mixture of benzene and ethyl acetate. Preliminary oscillation and Weissenberg photographs showed the crystal system to be orthorhombic with systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$, consistent with the space group $P2_12_12_1$. Unit-cell dimensions and their standard deviations were derived from a least-squares fit to the setting angles of 15 carefully centred reflections on a Syntex $P2_1$ automated diffractometer. The crystal density, measured by flotation in aqueous NaI solution, indicated four formula units per unit cell. The intensities for a nearly cubic crystal with edges of 0·3 mm were measured on the Syntex $P2_1$ diffractometer with Cu $K\alpha$ radiation. The data were collected in the θ–2θ scan mode. A set of 1142 independent intensities with $I \geq 1{\cdot}96\sigma(I)$ was used for the structure determination. The intensities were not corrected for absorption effects. An approximate absolute scale was determined by the method of Wilson (1942). The structure was solved by direct methods employing *MULTAN* (Germain, Main & Woolfson, 1971). All nonhydrogen atoms were found on the E map derived from the sign set with the highest figure of merit. Several cycles of isotropic and anisotropic refinement, minimizing the quantity $\sum(|F_o| - |F_c|)^2$, led to an R [$= \sum(|F_o| - |F_c|)/\sum|F_o|$] of 0·09. At this stage a difference Fourier map was computed and positional parameters were obtained for the 20 H atoms; the isotropic thermal parameters of the H atoms were approximately equal to those of the atoms to which they were bound. Three further cycles of refinement, employing anisotropic thermal parameters for the nonhydrogen atoms and holding the H atom parameters fixed, led to convergence (all shift/error values <0·3) and a final R value of 0·045. The final difference Fourier map was essentially featureless. Neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Final atomic positional parameters for the nonhydrogen atoms are collected in Table 1.*

Discussion. A view of the molecule projected along the y axis is shown in Fig. 1. The conformation of both dioxaphosphorinane rings is a flattened chair. The phosphoryl and thiophosphoryl bonds are equatorially sited. The flattening of the rings is illustrated by the two dihedral angles (Fig. 2) and the torsion angles (Fig. 3). The dihedral angles are almost identical in both the chairs: 33·5 (7) and 34·5 (9)° in the phosphorus part and 52·2 (8) and 50·4 (10)° in the carbon part of the chairs, and are typical for 1,3,2-dioxaphosphorinane rings (Bukowska-Strzyżewska & Dobrowolska, 1978). The flattening of the chair is not influenced by the comparatively short thiophosphoryl P=S bond.

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35742 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

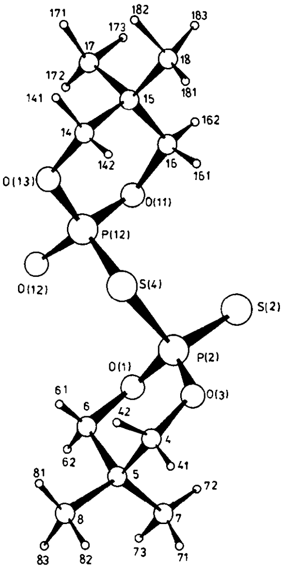

Fig. 1. The molecule projected along the y axis.

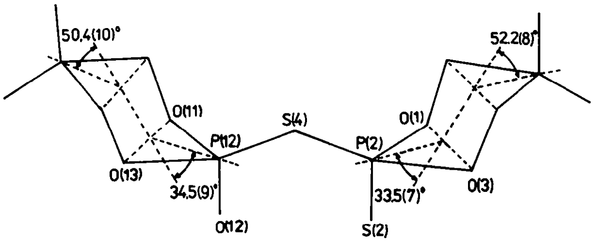

Fig. 2. The flattening of the ring.

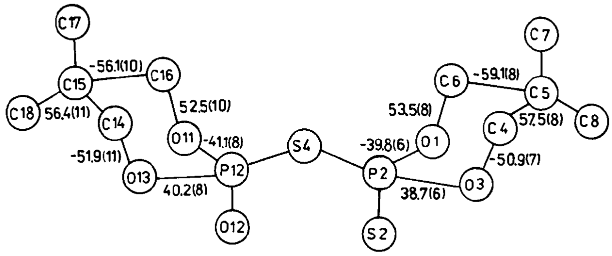

Fig. 3. The torsion angles (°).

The C_s symmetry of the rings is not destroyed by intermolecular forces. The asymmetry parameters of the rings, $\Delta C_s(2) = 1{\cdot}9$ and $\Delta C_s(12) = 0{\cdot}6°$, are very small. Intramolecular bond lengths and valency angles are given in Table 2. The average (within 2σ) length of the two bridging P—S bonds is 2·103 (4) Å, of the four intra-ring P—O bonds 1·575 (4) Å, of the four C—O bonds 1·454 (3) Å, of the four intra-ring C—C bonds 1·520 (2) Å and of the four inter-ring C—C bonds 1·537 (6) Å. The bond lengths found in the dioxaphosphorinane rings are consistent with the literature data cited above.

Table 2. *Bond lengths* (Å) *and angles* (°)

P(2)—S(2)	1·874 (3)	P(12)—O(12)	1·538 (7)
P(2)—O(1)	1·578 (5)	P(12)—O(11)	1·563 (8)
P(2)—O(3)	1·580 (5)	P(12)—O(13)	1·579 (8)
P(2)—S(4)	2·107 (3)	P(12)—S(4)	2·099 (3)
O(1)—C(6)	1·453 (10)	O(11)—C(16)	1·457 (12)
O(3)—C(4)	1·459 (9)	O(13)—C(14)	1·447 (13)
C(5)—C(4)	1·522 (10)	C(15)—C(14)	1·503 (15)
C(5)—C(6)	1·524 (11)	C(15)—C(16)	1·530 (15)
C(5)—C(7)	1·543 (11)	C(15)—C(17)	1·544 (14)
C(5)—C(8)	1·517 (12)	C(15)—C(18)	1·542 (16)
O(1)—P(2)—O(3)	105·9 (3)	O(11)—P(12)—O(13)	105·1 (4)
O(1)—P(2)—S(4)	107·5 (2)	O(11)—P(12)—S(4)	108·0 (3)
O(1)—P(2)—S(2)	112·5 (2)	O(11)—P(12)—O(12)	113·8 (4)
O(3)—P(2)—S(4)	99·5 (2)	O(13)—P(12)—S(4)	100·4 (3)
O(3)—P(2)—S(2)	113·8 (2)	O(13)—P(12)—O(12)	113·0 (4)
S(2)—P(2)—S(4)	116·3 (1)	O(12)—P(12)—S(4)	115·2 (3)
P(2)—O(1)—C(6)	118·9 (4)	P(12)—O(11)—C(16)	119·9 (5)
P(2)—O(3)—C(4)	119·8 (4)	P(12)—O(13)—C(14)	119·4 (7)
O(1)—C(6)—C(5)	111·8 (6)	O(11)—C(16)—C(15)	111·4 (8)
O(3)—C(4)—C(5)	111·8 (6)	O(13)—C(14)—C(15)	112·9 (9)
C(6)—C(5)—C(4)	108·6 (6)	C(16)—C(15)—C(14)	109·1 (9)
C(6)—C(5)—C(8)	109·3 (7)	C(16)—C(15)—C(17)	109·2 (8)
C(6)—C(5)—C(7)	110·6 (6)	C(16)—C(15)—C(18)	108·0 (8)
C(4)—C(5)—C(8)	107·7 (6)	C(14)—C(15)—C(17)	111·9 (9)
C(4)—C(5)—C(7)	110·2 (6)	C(14)—C(15)—C(18)	108·8 (9)
C(7)—C(5)—C(8)	110·5 (7)	C(18)—C(15)—C(17)	109·8 (9)
P(2)—S(4)—P(12)	103·2 (1)		

The literature data show that the phosphoryl P=O bond is strong, highly polar and rather short. The lengths observed previously are within the wide range 1·38–1·56 Å, with an average value of 1·462 Å (Corbridge, 1974). Shorter or longer than average P=O bonds have often been explained as resulting from a redistribution of the π bond amongst the other P—R bonds. The lengthening of this bond can also be caused by metal-complex formation or hydrogen bonding. The thiophosphoryl P=S bond is weaker and its relative ionic character is only about 8% compared with about 80% for P=O (Pauling, 1960). Most observed thiophosphoryl bond lengths range from 1·85 to 1·96 Å with an average value of 1·930 Å (Corbridge, 1974).

The P(12)—O(12) bond, 1·538 (7) Å, is distinctly longer and the P(2)—S(2), 1·874 (3) Å, shorter than the above-cited average values of phosphoryl and thiophosphoryl bonds. In spite of the fact that the difference Fourier synthesis did not show the maxima of electron density distribution which would indicate statistical exchange of the P=S with the P=O bond, we considered this possibility. However, in contrast to our earlier investigation of the structure of 2-oxo-2′-thioxobis(5,5-dimethyl-1,3,2-dioxaphosphorinanyl) oxide (III), in this case the refined occupancies of O(12) and S(2) are close to 1·0. The possibility that the observed abnormally long P—O and abnormally short P—S bonds may be due to statistical interchange was dismissed. None of the other isomers (I)–(III) showed such an abnormally long P=O bond: (I) P=O

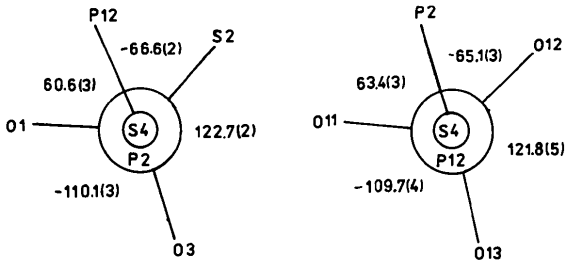

Fig. 4. Newman projections around the P(2)—S(4) and P(12)—S(4) bonds, showing torsion angles (°).

1·449 (11); (II) P=O 1·402 (14) and 1·426 (13); (III) P=O 1·45 (2) and 1·50 (5), and P=S 1·87 (5) and 1·78 (3). The comparatively long phosphoryl P(12)—O(12) and short thiophosphoryl P(2)—S(2) bonds of isomer (IV) are not accompanied by a shortening or elongation of the other P—O and P—S bonds in the PO_3S and PO_2S_2 tetrahedra.

The mutual orientation of both the tetrahedra is shown in Fig. 4 which represents the Newman projection around the bridging P(2)—S(4) and P(12)—S(4) bonds. The bridging plane P(2)—S(4)—P(12) divides nearly symmetrically the largest dihedral angles of the tetrahedra.

The molecular packing did not show a distinct shortening of intermolecular distances.

This research was supported by project MR-I-9 from the Polish Academy of Sciences.

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Structure of 17β-Hydroxy-7α-methyl-5-androsten-3-one (RMI 12,936)

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(*Received* 6 *October* 1980; *accepted* 2 *December* 1980)

Abstract. $C_{20}H_{30}O_2$, $M_r = 302{\cdot}2$, $D_m = 1{\cdot}19$, $D_x = 1{\cdot}19$ Mg m^{-3}, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 5{\cdot}970\,(2)$, $b = 14{\cdot}070\,(3)$, $c = 20{\cdot}015\,(3)$ Å, $U = 1681{\cdot}2$ Å^3. Final $R = 0{\cdot}029$ for 1294 independent reflexions. Rings *A* and *C* are observed in chair conformations whilst ring *B* approximates to the 8β,9α-half-chair form. Ring *D* approximates to an envelope conformation and an O(2)—H···O(1) hydrogen bond (2·85 Å) provides the head-to-tail linkage between hydroxy and carbonyl O atoms of adjacent molecules.

Introduction. The X-ray crystal structure of the title compound was undertaken as part of a programme to determine the conformational features of a number of related antiprogestational steroids. RMI 12,936 is an antiprogestational *and* an antiœstrogenic steroid and its antifertility activity has attracted attention (Kendle, 1979; Geddes, Kendle, Shanks & Steven, 1979). Of particular structural interest is the influence of the 7α methylation on ring conformation. Crystallographic data were obtained on an Enraf–Nonius CAD-4 automated diffractometer with Ni-filtered Cu *Kα*

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