literature data. The slight shortening of the C(sp^3)—C(sp^3) bond [1·473 (26) Å] is probably due to the large B_{33} values of these atoms.

The imide ring is ideally planar. Typical and identical values of the N—C(sp^2) bond lengths [1·387 (9) Å] and almost identical (within the 2σ range) C(sp^2)—O bond lengths are observed. The symmetrical π delocalization within C=O and C—N bonds is due to the ideal planarity of the ring. The phenyl ring perpendicular to the imide ring is ideally planar. The average C—C bond length [1·399 (8) Å] is typical for the phenyl ring and the average C—C—C bond angle is 120·0 (6)°. The bond angle at C(11) substituted by the methyl group is decreased to the value 114·1 (6)° and that at C(10) substituted by the imide ring is increased to the value 125·9 (6)°.

The molecular packing is comparatively loose. The coefficient of molecular packing expressed according to Kitaigorodsky (1973) as $w = (\sum_i \Delta V_i)/V$ is only 0·69; ($\sum_i \Delta V_i$ is the volume of molecules, limited by the van der Waals radii, contained in the unit cell and V is the volume of the unit cell). Unusually long distances along the z axis are observed between all atoms situated on the mirror planes. All these distances exceed $\frac{1}{2}c = 4·356$ Å. These long intermolecular distances result from the perpendicular position of the dimethylphenyl ring with respect to the mirror plane. The intramolecular distance C(14)$\cdots$C(14') determines the value of c as 8·712 (1) Å and it is this value that determines the long intermolecular distances between atoms on the mirror planes. The shortest intermolecular distance along the z axis is 3·836 (18) Å [between C(2) and C(5') – the latter deviating statistically from the mirror plane]. The very loose packing of the dithiacyclohexene and imide rings results in strong thermal oscillations of C(4), C(5), S and O along the z axis. Fig. 2 shows the packing.
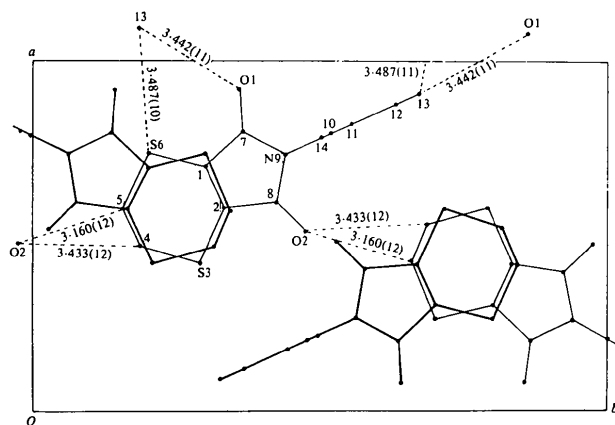
Fig. 2. Molecular packing. (Distances in Å.)

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

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Abstract. $C_{10}H_{20}O_6P_2S$, orthorhombic, *Pbca*, $a = 27·949$ (5), $b = 9·893$ (2), $c = 11·519$ (3) Å, $V = 3185·0$ Å^3, $D_x = 1·37$, $D_m = 1·38$ Mg m^{-3}, $Z = 8$, $F(000) = 1392$, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 3·72 mm^{-1}. The crystals are isostructural with the analogous pyrophosphate [Bukowska-Strzyżewska & Dobrowolska (1978). *Acta Cryst.* B**34**, 1357–1360]. Disorder of the S(2) and O(12) atoms was observed, with the P=S and P=O bonds statistically inter-

changed in the molecule. The S(2) and O(12) oc-cupancy of the major component is 0·768 (9). The structure was refined by least-squares methods with anisotropic temperature factors to an R of 0·055 for 1640 independent reflections. The dioxaphosphorinane rings have partially flattened chair conformations with the double-bonded atom in an equatorial and the linking O atom in an axial position. Asymmetry parameters calculated for the dioxaphosphorinane ring are $\Delta C_s(2–5) = 2·4$, $\Delta C_s(12–15) = 0·2°$.

Introduction. Several structures of bicyclic organic pyro- and thiopyrophosphates have been studied by us (Bukowska-Strzyżewska, Dobrowolska, Michalski, Młotkowska & Skoweranda, 1976; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Bukowska-Strzyżewska & Dobrowolska, 1978).

The investigated crystals of
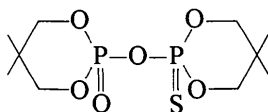
are isostructural with those of bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) oxide (Bukowska-Strzyżewska & Dobrowolska, 1978).

The compound was crystallized from a mixture of benzene and ligroin.

The density was measured by flotation in aqueous NaI solution. The cell parameters and intensities were measured for a single crystal (ground to a sphere of 0·15 mm radius), using an automatic CAD-4 single-crystal diffractometer (Cu $K\alpha$, Ni-filtered radiation), by a $\theta–2\theta$ scan. The intensities were measured at the Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University of Kraków. The averaged data were corrected for Lorentz and polarization effects and for absorption ($\mu = 3·72$ mm^{-1}). The atom coordinates used to calculate the phases and Fourier syntheses, except for those of O(2) and O(12), were those from isostructual bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) oxide. The structure was refined by isotropic ($R = 13·6\%$) and anisotropic full-matrix least-squares methods. The difference Fourier synthesis showed all the H atoms, which were refined with isotropic thermal parameters. The R value was 6·8%. The P(2)–S(2) and P(12)–O(12) lengths obtained at this stage of 1·842 (2) and 1·589 (3) Å were clearly too short and too long respectively for P=S and P=O bonds. The difference Fourier synthesis showed roughness of the electron density distribution indicating the possibility of statistical substitution of the P=S by the P=O bond. The parameters of these disordered S and O atoms

were further refined starting from occupancy factors of 0·5. The occupancy factors obtained for S(2) and O(12) are 0·768 (9), for S(20) and O(120) 0·232 (9). The final full-matrix least-squares refinement of the whole structure gave $R = 0·055$ and the atomic coordinates listed in Table 1.* Form factors for neutral atoms were taken from Doyle & Turner (1968) and for H from *International Tables for X-ray Crystallography* (1962).

Table 1. *Atomic positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	B (Å^2)
O(4)	1187 (1)	6135 (3)	791 (3)	5·2 (2)
P(2)	1194 (1)	4549 (1)	511 (1)	4·7 (8)
O(1)	656 (1)	4194 (3)	311 (3)	5·0 (2)
O(3)	1335 (1)	3953 (4)	1723 (3)	5·8 (2)
S(2)	1615 (2)	4002 (6)	−662 (5)	6·2 (1)
O(120)	1471 (14)	4248 (49)	−577 (44)	9·5 (4)
C(4)	993 (2)	3993 (6)	2687 (5)	6·1 (3)
C(5)	511 (2)	3441 (5)	2313 (5)	5·3 (4)
C(6)	329 (2)	4269 (6)	1299 (6)	6·0 (3)
C(7)	174 (3)	3622 (8)	3348 (7)	9·9 (5)
C(8)	546 (2)	1951 (6)	1979 (6)	6·4 (4)
P(12)	1153 (0)	7458 (2)	1 (1)	4·7 (8)
O(12)	773 (8)	7392 (25)	−856 (18)	8·1 (4)
S(20)	700 (11)	7580 (33)	−1082 (25)	5·9 (4)
O(11)	1669 (1)	7648 (4)	−490 (3)	5·0 (2)
O(13)	1089 (1)	8571 (4)	937 (4)	5·2 (2)
C(14)	1478 (2)	8795 (6)	1765 (5)	5·7 (3)
C(15)	1949 (2)	9061 (6)	1130 (5)	5·0 (3)
C(16)	2055 (2)	7864 (6)	322 (5)	5·5 (3)
C(17)	2343 (2)	9133 (8)	2039 (6)	7·7 (4)
C(18)	1922 (2)	10363 (6)	424 (7)	7·6 (4)
H(183)	223 (2)	1048 (5)	−13 (4)	7·0 (19)
H(182)	187 (2)	1105 (5)	104 (4)	7·0 (18)
H(181)	165 (1)	1052 (5)	−31 (4)	11·4 (18)
H(83)	20 (1)	154 (4)	171 (3)	5·3 (15)
H(82)	67 (7)	153 (6)	270 (5)	9·2 (20)
H(81)	79 (2)	178 (5)	129 (4)	5·0 (16)
H(173)	268 (1)	936 (4)	159 (3)	5·0 (17)
H(172)	237 (1)	820 (4)	263 (4)	5·4 (14)
H(171)	229 (1)	1000 (4)	267 (4)	6·7 (17)
H(73)	−13 (2)	323 (5)	308 (4)	8·6 (24)
H(72)	7 (2)	455 (6)	367 (5)	8·1 (25)
H(71)	23 (2)	309 (5)	391 (4)	11·9 (23)
H(162)	235 (1)	818 (4)	−15 (3)	2·5 (14)
H(161)	208 (1)	688 (4)	78 (3)	4·4 (13)
H(62)	0 (2)	402 (5)	83 (4)	9·6 (18)
H(61)	29 (2)	531 (4)	146 (4)	7·2 (16)
H(142)	153 (1)	780 (4)	220 (4)	3·2 (14)
H(141)	134 (1)	954 (4)	229 (3)	5·2 (14)
H(42)	93 (1)	513 (5)	307 (3)	6·9 (17)
H(41)	114 (2)	338 (5)	339 (4)	7·3 (18)

Discussion. A view of the major-component molecule projected along the axis perpendicular to the P—O—P plane is shown in Fig. 1. Intramolecular bond lengths and valency angles are listed in Table 2. The occupancy factors for disordered atoms are given in brackets after the symbols of the atoms. The angle between the bridge bonds P(2)—O(4) and P(12)—O(4) is 133·6 (2)° [slightly greater than that in the isostructural pyrophosphate where it is 132·0 (8)°]. The P—O bridge bond lengths vary only by 0·004 Å (1σ), with a mean of 1·599 Å. They are slightly shorter than in the pyrophosphate where they are 1·647 (11) and 1·612 (11) Å. The dioxaphosphorinane rings have deformed (flattened in the phosphorus part) chair conformations. The bridge atom, O(4), takes the axial position in relation to both the rings.

The mutual orientation of the two phosphorus tetrahedra is shown in Fig. 2, which gives Newman projections around the P(2)—O(4) and P(12)—O(4) bonds, taking into consideration the disorder of the
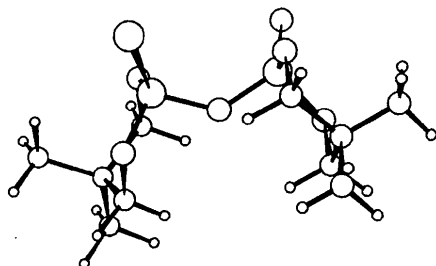
S(2) and O(12) atoms. The orientation is approximately staggered. The torsion angles P(2)—O(4)—P(12)—O(12) and P(2)—O(4)—P(12)—S(20) are 48·3 (12) and 49·6 (12)°, respectively, and P(2)—O(4)—P(12)—O(11) is 78·6 (3)°. In the other ring the angles P(12)—O(4)—P(2)—S(2) and P(12)—O(4)—P(2)—O(120) are 47·9 (4) and 37·3 (18)°, respectively, and P(12)—O(4)—P(2)—O(1) is 80·1 (3)°. The torsion angles, their average values and the asymmetry parameters of the dioxaphosphorinane rings are given in Fig. 3. Both rings have a nearly ideal mirror plane, $\Delta C_s(2–5) = 2·4$, $\Delta C_s(12–15) = 0·2°$. The ring containing P(12) is less flattened. The dihedral angle between the P(12)—O(11)—O(13) and O(11)—O(13)—C(14)—C(16) planes is 38·4 (3)°, while in the ring containing P(2) this angle is 32·8 (3)°. In other structures a different flattening of the phosphorus part of the ring has been observed. The dihedral angle mentioned above can vary from 3·7 to 45·7° (Drew & Rodgers, 1972; Dutasta, Grand & Robert, 1974). The flattening of these rings in the title compound is very similar to that in the isostructural pyrophosphate where the dihedral angles are 36°. It seems that the substitution of the P=O by the P=S bond slightly increases the flattening of the dioxaphosphorinane rings. Good agreement between the lengths of analogous bonds in the two rings is observed.

Fig. 1. The molecule projected along the axis perpendicular to the P—O—P plane.

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

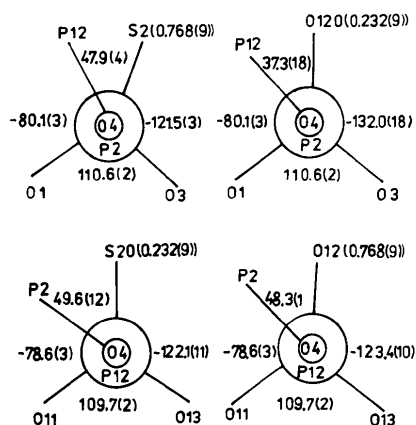|			
P(2)—S(2) [0·768 (9)]	1·871 (5)	P(12)—S(20) [0·232 (9)]	1·78 (3)
P(2)—O(1)	1·562 (4)	P(12)—O(11)	1·560 (4)
P(2)—O(3)	1·565 (4)	P(12)—O(13)	1·552 (4)
P(2)—O(4)	1·601 (3)	P(12)—O(4)	1·597 (4)
P(2)—O(120) [0·232 (9)]	1·50 (5)	P(12)—O(12) [0·768 (9)]	1·45 (2)
O(1)—C(6)	1·461 (7)	O(11)—C(16)	1·443 (7)
O(3)—C(4)	1·465 (7)	O(13)—C(14)	1·464 (7)
C(5)—C(4)	1·517 (9)	C(15)—C(14)	1·528 (8)
C(5)—C(6)	1·514 (8)	C(15)—C(16)	1·534 (8)
C(5)—C(7)	1·531 (10)	C(15)—C(17)	1·522 (9)
C(5)—C(8)	1·527 (8)	C(15)—C(18)	1·526 (9)
O(1)—P(2)—O(3)	106·8 (2)	O(11)—P(12)—O(13)	105·9 (2)
O(1)—P(2)—O(4)	103·8 (2)	O(11)—P(12)—O(4)	104·5 (2)
O(1)—P(2)—S(2)	115·6 (2)	O(11)—P(12)—O(12)	115·8 (8)
O(3)—P(2)—O(4)	101·1 (2)	O(13)—P(12)—O(4)	101·1 (2)
O(3)—P(2)—S(2)	112·2 (2)	O(13)—P(12)—S(20)	110·8 (10)
O(4)—P(2)—S(2)	115·9 (2)	O(4)—P(12)—S(20)	119·8 (10)
O(120)—P(2)—O(4)	111·6 (18)	O(12)—P(12)—O(4)	113·2 (9)
O(120)—P(2)—O(1)	109·2 (16)	S(20)—P(12)—O(11)	113·3 (10)
O(120)—P(2)—O(3)	122·7 (18)	O(12)—P(12)—O(13)	114·8 (9)
P(2)—O(1)—C(6)	118·4 (3)	P(12)—O(11)—C(16)	118·2 (3)
P(2)—O(3)—C(4)	120·1 (3)	P(12)—O(13)—C(14)	118·3 (3)
O(1)—C(6)—C(5)	111·3 (4)	O(11)—C(16)—C(15)	111·3 (4)
O(3)—C(4)—C(5)	110·7 (5)	O(13)—C(14)—C(15)	110·7 (5)
C(6)—C(5)—C(4)	108·8 (5)	C(16) C(15) C(14)	108·9 (5)
C(6)—C(5)—C(8)	110·4 (5)	C(16)—C(15)—C(18)	109·8 (5)
C(6)—C(5)—C(7)	109·3 (5)	C(16)—C(15)—C(17)	108·3 (5)
C(4)—C(5)—C(8)	111·2 (5)	C(14)—C(15)—C(18)	111·0 (5)
C(4)—C(5)—C(7)	106·5 (5)	C(14)—C(15)—C(17)	107·6 (5)
C(7)—C(5)—C(8)	110·4 (5)	C(17)—C(15)—C(18)	111·2 (5)
P(2)—O(4)—P(12)	133·6 (2)		

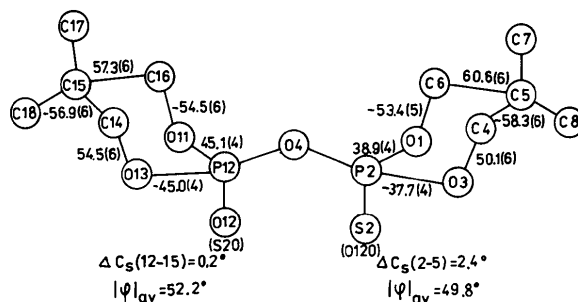Fig. 2. Newman projections around the P(2)—O(4) and P(12)—O(4) bonds, showing the relevant torsion angles (°).

Fig. 3. Torsion angles (°).

The maximum difference between the P—O bond lengths of the rings is 0·013 Å (3σ) and the mean length is 1·560 Å. The four C—O, the four $C(sp^2)$—$C(sp^3)$ and the four $C(sp^3)$—$C(sp^3)$ bond lengths vary by maximum values of 0·021 (3σ), 0·020 (2σ) and 0·009 (2σ) Å with mean lengths of 1·458, 1·523 and 1·527 Å respectively. The C—H bond lengths vary by a maximum of 0·375 Å (9σ) with a mean length of 1·07 Å. The P(2)—O(120) and P(12)—O(12) bond lengths are identical within the observed error with a mean value 1·47 Å. Only the P(2)—S(2) = 1·871 (5) and P(12)—S(20) = 1·78 (3) Å bonds are distinctly different, being shorter than in other organic thiophosphates. In other structures the length of this bond varies from 1·884 to 1·942 Å (Wieczorek, Sheldrick, Karolak-Wojciechowska, Mikołajczyk &

Ziemnicka, 1979; Wieczorek, Karolak-Wojcie-chowska, Mikołajczyk & Witczak, 1978). The shortening of these bonds could be partly due to the difficulty in the refinement of the disordered and partially overlapping atoms S(20) and O(12), and S(2) and O(120).

The molecular packing (Fig. 4) shows a distinct shortening of the S(20)—H and S(2)—H intermolecular distances.

Fig. 4. The molecular packing, showing some intermolecular distances (Å).

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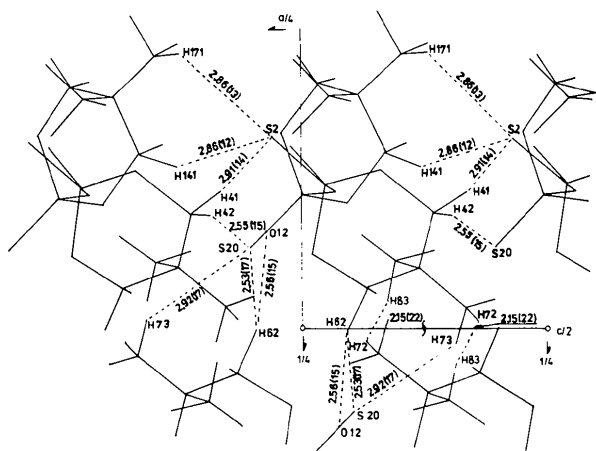
Neutron Diffraction Study of 2-Nitro-1,3-indandione Dihydrate*

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Abstract. $H_5O_2^+.C_9H_4NO_4^-$, monoclinic, $P2_1/c$, $Z = 4$, $a = 9·633$ (1), $b = 5·176$ (1), $c = 19·713$ (2) Å, $\beta = 102·59$ (1)°; neutron wavelength 1·210 Å, μ(measured) = 0·158 mm⁻¹. Refinement with 2652 data recorded at 294 K gave a final $R_w(F^2) = 0·050$. The $H_5O_2^+$ complex is an aquaoxonium ion, $H_3O^+.H_2O$. The O···O distance in the internal H bond is 2·477 (2) Å; the O—H and H···O distances are 1·087 (3) and 1·390 (3) Å respectively. The $H_5O_2^+$ complex is H bonded to O in four different nitronate ions. One of the water H atoms participates in a bifurcated H bond.