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The Crystal and Molecular Structures of Six- and Seven-Membered-Ring Organophosphorus Compounds. 1,3,2-Dioxaphosphorinanes and 1,5-Dihydro-1,4,3-benzodioxaphosphins

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The structures of four six- and seven-membered-ring organophosphorus molecules have been determined by direct methods. In these molecules, the P atom is four-coordinate $\begin{array}{c} \text{O} \\ \diagdown \\ \text{P}=\text{S} \\ \diagup \\ \text{O} \end{array}$, with $R = \text{CH}_3$ or $\text{N}(\text{CH}_3)_2$.

The four molecules adopt a chair conformation with the P=S bond in the axial orientation. The flattening of the ring is smaller in the seven- than in the six-membered rings. The O–P–O and C–O–P ring angles show an increase of *ca* 2 and 3°, respectively, in going from the six- to the seven-membered ring.

Introduction

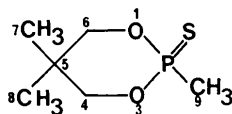
In contrast to several structure determinations of 2-*R*-2-oxo- or 2-thiono-1,3,2-dioxaphosphorinanes (Corbridge, 1974; Silver & Rudman, 1972; Drew & Rodgers, 1972; Saenger & Mikolajczyk, 1973; Cook & White, 1976; Bukowska-Strzyżewska, Michalski, Młotkowska & Skoweranda, 1976; Grand & Robert, 1975) little attention has been paid to the structure determination of the corresponding seven-membered rings. To our knowledge, only one determination has been made of a 1,3,2-dioxaphospha seven-membered ring, tetramethylenephosphoric acid (Coulter, 1975).

Solutions of 2-oxo- and 2-thiono-1,3,2-dioxaphos-

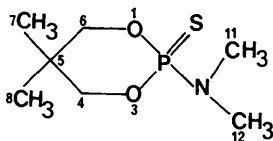
phorinanes have also been investigated by NMR spectroscopy (Bentrude & Hargis, 1970; Katritzky, Nesbit, Michalsky, Tulinowski & Zwierzak, 1970; Bartle, Edmundson & Jones, 1967; Bentrude, Tan & Yee, 1972; Bentrude & Tan, 1973; Finocchiaro, Recca, Bentrude, Tan & Yee, 1976; Dutasta, Grand, Robert & Taieb, 1974) but only a few deal with the NMR spectral analysis of the corresponding seven-membered rings (Sato & Goto, 1973; Guimaraes, Robert & Taieb, 1977). We present the solid-state structure determination of four 2-thiono-1,3-dioxaphosphorus molecules: two six- (I, II) and two seven-membered-ring (III, IV) molecules in which the same *R* groups are attached to the P atoms. The conformation of (I) has been reported (Dutasta, Grand & Robert, 1974).

The present analysis was undertaken for three main

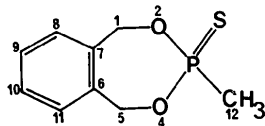
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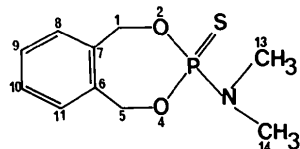
(I) 2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane



(II) 2-Thiono-2-N-dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane



(III) 3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin



(IV) 3-Thiono-3-N-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin

reasons. Firstly, to examine the bond-angle and bond-length changes in going from a six- to a seven-membered ring in which the same *R* groups are attached to the P atom; secondly, to compare the *R* group orientation in the six- and seven-membered rings; thirdly, to examine the modification of the NMR spectral parameters [^{31}P chemical shift, $^3J(\text{POCH})$ and $^1J(\text{PC})$ coupling constants] with the structural parameters. The full set of NMR spectral parameters of several seven-membered-ring organophosphorus compounds, including (III) and (IV), are reported in separate studies (Guimaraes, 1977; Guimaraes, Robert & Taieb, 1977).

Experimental

(I)–(IV) were prepared by standard methods. The corresponding three-coordinate P compound was first obtained by reacting dichloromethylphosphine with 2,2-dimethyl-1,3-propanediol or with phthalyl alcohol for (I) and (III) respectively. Dichloromethylphosphine

was replaced by hexamethylphosphorus triamide for (II) and (IV). The 2-thiono derivatives were obtained by direct addition of S to the three-coordinate P compounds (Edmundson, 1962). The compounds were purified by chromatography on a silica column with benzene as eluant.

Single crystals of (II) and (III) were grown by cooling from benzene. For (I) and (IV), crystals were obtained from benzene–hexane and carbon tetrachloride respectively. The crystal data are summarized in Table 1.

The space groups of (I), (III) and (IV) are unambiguously assigned by the systematic absences: (I):

Table 2. Six-membered rings: fractional coordinates ($\times 10^4$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane (I)			
P	−223 (1)	282 (1)	707 (2)
O(1)	1002 (3)	531 (2)	1997 (5)
O(3)	−533 (2)	1182 (2)	−682 (6)
C(4)	443 (4)	1547 (3)	−2122 (8)
C(5)	1575 (4)	1757 (3)	−707 (9)
C(6)	1983 (4)	887 (3)	537 (10)
C(7)	2596 (5)	2045 (4)	−2367 (10)
C(8)	1313 (5)	2525 (3)	1060 (10)
S	−140 (1)	−802 (1)	−1156 (2)
C(9)	−1310 (5)	283 (4)	2965 (10)
2-Thiono-2-N-dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane (II)			
P	3670 (1)	2500	590 (2)
O(1)	3161 (2)	4060 (5)	−17 (5)
C(6)	2369 (3)	4065 (8)	551 (7)
C(5)	1946 (5)	2500	−94 (11)
C(7)	1127 (6)	2500	697 (16)
C(8)	1880 (6)	2500	−2028 (11)
S	3913 (1)	2500	2947 (3)
N	4392 (4)	2500	−680 (9)
C(11)	4265 (8)	2500	−2544 (14)
C(12)	5195 (6)	2500	−173 (18)

Table 1. Crystal data

(I)	(II)	(III)	(IV)
2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane	2-Thiono-2-N-dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane	3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin	3-Thiono-3-N-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin
$\text{C}_6\text{H}_{13}\text{O}_2\text{PS}$	$\text{C}_7\text{H}_{16}\text{NO}_2\text{PS}$	$\text{C}_9\text{H}_{11}\text{O}_2\text{PS}$	$\text{C}_{10}\text{H}_{14}\text{NO}_2\text{PS}$
FW 180.20	FW 209.24	FW 245.19	FW 243.26
Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group $P2_12_12_1$	Space group $Pnma$	Space group $P2_1/c$	Space group $P2_1/c$
<i>Z</i> 4	<i>Z</i> 4	<i>Z</i> 4	<i>Z</i> 4
<i>F</i> (000) 384	<i>F</i> (000) 448	<i>F</i> (000) 448	<i>F</i> (000) 512
<i>a</i> 10.969 (1) Å	<i>a</i> 17.509 (5) Å	<i>a</i> 9.414 (2) Å	<i>a</i> 7.696 (2) Å
<i>b</i> 14.656 (1)	<i>b</i> 7.952 (1)	<i>b</i> 9.799 (2)	<i>b</i> 7.621 (2)
<i>c</i> 5.797 (1)	<i>c</i> 7.936 (2)	<i>c</i> 11.153 (2)	<i>c</i> 21.599 (4)
β 95.75 (1)°		β 95.75 (1)°	β 106.53 (2)°
<i>V</i> 931.9 Å ³	<i>V</i> 1104.9 Å ³	<i>V</i> 1023.66 Å ³	<i>V</i> 1214.45 Å ³
<i>D_m</i> 1.23 (5) g cm ^{−3}	<i>D_m</i> 1.23 (5) g cm ^{−3}	<i>D_m</i> 1.57 (5) g cm ^{−3}	<i>D_m</i> 1.34 (5) g cm ^{−3}
<i>D_x</i> 1.284	<i>D_x</i> 1.257	<i>D_x</i> 1.590	<i>D_x</i> 1.330

$P2_12_1$ ($h00$, $0k0$ and $00l$ absent for h , k or l odd); (III) and (IV): $P2_1/c$ ($h0l$ absent for l odd, $0k0$ for k odd). The cell dimensions were refined from the diffractometer data. Intensities were collected with Ni-filtered $\text{Cu } K\alpha$ radiation for (I) and (III), and $\text{Mo } K\alpha$

radiation for (II) and (IV). The number of intensities [$3^\circ < \theta < 70^\circ$ for (I) and (III); $3^\circ < \theta < 30^\circ$ for (II) and (IV)] were 1071, 1859, 1993 and 2360 for (I), (II), (III) and (IV) respectively. During data collection, a check reflexion was recorded periodically [291 (I), 313 (II), 133 (III) and 123 (IV)]. They showed no fall in intensity during the experiments. The intensities were measured by the five-point method (Troughton, 1969) and corrected for Lorentz and polarization factors, but not for absorption. Of the intensities collected for (I), (II), (III) and (IV), 992, 827, 1385 and 1474, respectively, were judged observed after

Table 3. *Seven-membered rings: fractional coordinates ($\times 10^4$) with standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin (III)			
P	6655 (1)	6728 (2)	2818 (2)
O(2)	6005 (1)	5880 (2)	3855 (2)
O(4)	7843 (2)	5768 (2)	2356 (2)
C(5)	9071 (3)	5383 (3)	3194 (2)
C(6)	8742 (3)	4171 (3)	3936 (2)
C(7)	7732 (3)	4255 (3)	4785 (2)
C(1)	6931 (3)	5551 (3)	4952 (2)
C(8)	7481 (3)	3112 (3)	5467 (2)
C(9)	8191 (4)	1899 (3)	5309 (3)
C(10)	9176 (4)	1820 (3)	4474 (3)
C(11)	9439 (3)	2956 (3)	3791 (2)
S	7332 (1)	8514 (1)	3318 (1)
C(12)	5272 (3)	6632 (3)	1621 (3)

3-Thiono-3-*N*-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin (IV)

P	4955 (5)	8040 (2)	8626 (1)
O(2)	6823 (5)	7843 (5)	8454 (2)
O(4)	4947 (5)	10034 (6)	8837 (2)
C(5)	6308 (8)	10684 (9)	9431 (3)
C(6)	8026 (7)	11202 (8)	9269 (3)
C(7)	9094 (7)	9964 (8)	9051 (3)
C(1)	8543 (8)	8042 (8)	8969 (3)
C(8)	10705 (8)	10470 (9)	8933 (3)
C(9)	11289 (8)	12214 (10)	9025 (3)
C(10)	10257 (9)	13434 (9)	9245 (3)
C(11)	8605 (8)	12951 (9)	9358 (3)
S	4626 (2)	6374 (3)	9252 (1)
N	3443 (7)	8019 (8)	7934 (3)
C(13)	3547 (12)	9394 (14)	7429 (4)
C(14)	1995 (0)	6752 (12)	7741 (4)

Table 4. *Six-membered rings: bond distances (Å) with standard deviations in parentheses*

2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane (I)			
P—O(1)	1.581 (3)	P—O(3)	1.582 (3)
O(3)—C(4)	1.458 (6)	O(1)—C(6)	1.465 (6)
C(4)—C(5)	1.520 (6)	C(5)—C(6)	1.532 (6)
C(5)—C(7)	1.536 (6)	C(5)—C(8)	1.549 (6)
P—S	1.924 (2)	P—C(9)	1.771 (5)
2-Thiono-2- <i>N</i> -dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane (II)			
P—O(1)	1.601 (4)	P—O(3)	1.601 (4)
O(3)—C(4)	1.458 (7)	O(1)—C(6)	1.458 (7)
C(4)—C(5)	1.536 (8)	C(5)—C(6)	1.536 (8)
C(5)—C(7)	1.566 (13)	C(5)—C(8)	1.539 (11)
P—S	1.919 (3)	P—N	1.616 (8)
N—C(11)	1.496 (13)	N—C(12)	1.462 (13)

Table 5. *Six-membered rings: bond angles ($^\circ$) with standard deviations in parentheses*

2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane (I)			
P—O(3)—C(4)	116.0 (2)	P—O(1)—C(6)	115.7 (3)
O(3)—C(4)—C(5)	111.4 (4)	O(1)—C(6)—C(5)	110.7 (3)
O(1)—P—S	114.6 (1)	O(3)—P—S	114.4 (1)
O(1)—P—C(9)	102.9 (2)	O(3)—P—C(9)	103.4 (2)
C(4)—C(5)—C(7)	110.6 (4)	C(6)—C(5)—C(7)	110.4 (4)
C(4)—C(5)—C(8)	108.3 (4)	C(6)—C(5)—C(8)	108.1 (4)
O(1)—P—O(3)	103.4 (1)	C(4)—C(5)—C(6)	108.9 (3)
C(7)—C(5)—C(8)	110.5 (4)	S—P—C(9)	116.6 (2)
2-Thiono-2- <i>N</i> -dimethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane (II)			
P—O(3)—C(4)	116.0 (5)	P—O(1)—C(6)	116.0 (5)
O(3)—C(4)—C(5)	110.6 (5)	O(1)—C(6)—C(5)	110.6 (5)
O(1)—P—S	114.6 (2)	O(3)—P—S	114.6 (2)
O(1)—P—N	104.3 (2)	O(3)—P—N	104.3 (2)
C(4)—C(5)—C(7)	107.9 (5)	C(6)—C(5)—C(7)	107.9 (5)
C(4)—C(5)—C(8)	111.7 (5)	C(6)—C(5)—C(8)	111.7 (5)
P—N—C(11)	125.5 (7)	P—N—C(12)	120.0 (7)
O(1)—P—O(3)	101.5 (5)	C(4)—C(5)—C(6)	108.3 (7)
C(7)—C(5)—C(8)	109.3 (8)	S—P—N	115.8 (3)
C(11)—N—C(12)	114.5		

Table 6. *Seven-membered rings: bond distances (Å) with standard deviations in parentheses*

3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin (III)			
P—O(2)	1.595 (2)	P—O(4)	1.587 (2)
O(4)—C(5)	1.461 (3)	O(2)—C(1)	1.465 (3)
C(5)—C(6)	1.498 (3)	C(1)—C(7)	1.498 (3)
C(6)—C(11)	1.377 (3)	C(7)—C(8)	1.387 (3)
C(8)—C(9)	1.384 (4)	C(10)—C(11)	1.385 (4)
C(6)—C(7)	1.411 (3)	C(9)—C(10)	1.381 (4)
P—S	1.925 (1)	P—C(12)	1.771 (3)
3-Thiono-3- <i>N</i> -dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin (IV)			
P—O(2)	1.591 (4)	P—O(4)	1.587 (4)
O(4)—C(5)	1.491 (6)	O(2)—C(1)	1.474 (7)
C(5)—C(6)	1.514 (8)	C(1)—C(7)	1.522 (8)
C(6)—C(11)	1.401 (8)	C(7)—C(8)	1.390 (8)
C(8)—C(9)	1.399 (9)	C(10)—C(11)	1.409 (9)
C(6)—C(7)	1.416 (8)	C(9)—C(10)	1.392 (9)
P—S	1.923 (2)	P—N	1.612 (5)
N—C(13)	1.443 (8)	N—C(14)	1.508 (9)

Table 7. *Seven-membered rings: bond angles (°) with standard deviations in parentheses*

3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin (III)			
P—O(2)—C(1)	118.7 (1)	P—O(4)—C(5)	118.9 (2)
O(2)—C(1)—C(7)	110.3 (2)	O(4)—C(5)—C(6)	111.4 (2)
C(5)—C(6)—C(7)	121.0 (2)	C(1)—C(7)—C(6)	121.0 (2)
C(6)—C(7)—C(8)	118.9 (2)	C(7)—C(6)—C(11)	119.4 (2)
C(7)—C(8)—C(9)	120.9 (3)	C(6)—C(11)—C(10)	121.1 (2)
C(8)—C(9)—C(10)	120.0 (3)	C(9)—C(10)—C(11)	119.7 (3)
C(5)—C(6)—C(11)	119.6 (2)	C(1)—C(7)—C(8)	120.1 (2)
S—P—O(2)	113.8 (1)	S—P—O(4)	114.7 (1)
O(2)—P—C(12)	102.3 (1)	O(4)—P—C(12)	102.3 (1)
O(2)—P—O(4)	105.1 (9)	S—P—C(12)	117.6 (1)
3-Thiono-3- <i>N</i> -dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin (IV)			
P—O(2)—C(1)	119.4 (4)	P—O(4)—C(5)	120.4 (3)
O(2)—C(1)—C(7)	110.4 (5)	O(4)—C(5)—C(6)	109.5 (5)
C(5)—C(6)—C(7)	122.1 (5)	C(1)—C(7)—C(6)	120.8 (5)
C(6)—C(7)—C(8)	120.6 (6)	C(7)—C(6)—C(11)	119.1 (6)
C(7)—C(8)—C(9)	120.3 (6)	C(6)—C(11)—C(10)	119.5 (6)
C(8)—C(9)—C(10)	119.5 (6)	C(9)—C(10)—C(11)	121.0 (6)
C(5)—C(6)—C(11)	118.8 (5)	C(1)—C(7)—C(8)	118.6 (5)
S—P—O(2)	114.2 (2)	S—P—O(4)	114.7 (2)
O(2)—P—N	104.2 (3)	O(4)—P—N	102.4 (3)
P—N—C(13)	124.7 (5)	P—N—C(14)	119.4 (5)
C(13)—N—C(14)	115.9 (6)	O(2)—P—O(4)	103.6 (2)

correction. The structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971). Least-squares refinement, with *ORFLS* (Busing & Levy, 1959) (P, O, C, N, S anisotropic) reached an $R = \Sigma |F_o - F_c| / \Sigma |F_o|$ of 0.052, 0.033 and 0.065 and an $R_w = [\Sigma \omega(F_o - F_c)^2 / \Sigma \omega F_o^2]^{1/2}$ of 0.074, 0.036 and 0.079 for (I), (III) and (IV) respectively.

For (II), solution of the structure began with *MULTAN* in the noncentrosymmetric space group $Pna2_1$. A set of 206 reflexions with $E > 1.4$ was used. The set of phases with the highest figures of merit gave a structure in which all the non-hydrogen atoms were located. R and R_w reached the values 0.076 and 0.115 respectively, but some important discrepancies appeared in the corresponding bond lengths and angles. Refinement in $Pnma$ reduced R and R_w to 0.064, and 0.097 respectively. Intensity statistics were not particularly helpful in deciding the space group since they

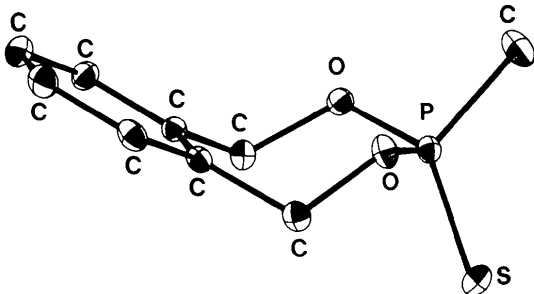


Fig. 1. 3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin.

were intermediate between centrosymmetric and non-centrosymmetric values. Positional parameters are listed in Tables 2 and 3, while Tables 4–7 contain bond distances and angles.*

Molecular geometry

In the solid state, the six-membered ring (I) and the seven-membered rings (III) (Fig. 1) and (IV) (Fig. 2) adopt a chair conformation which departs only slightly from the C_s symmetry observed in (II). Defining the plane of symmetry as the best least-squares plane through P, S, C(9), C(5), C(7) and C(8) for (I), and through P, S, C(12) or N for (III) and (IV), the equations of the corresponding planes with distances to the ring atoms are shown in Table 8.

The general shape of the ring may be characterized by two dihedral angles defined by the best least-squares plane through the four central atoms of the ring and the O—P—O plane on the one hand (α_1) and the plane of the remaining C atoms on the other (α_2). The corresponding values are

	(I)	(II)	(III)	(IV)
α_1 (°)	45.7	46.7	52.5	53.1
α_2 (°)	51.9	52.7	59.4	59.4

The flattening of the ring at the P end is smaller in the seven- than in the six-membered ring.

In the four molecules under study, the P=S bond adopts the axial orientation in the solid state. However, in solution these molecules show a chair–chair equilibrium in which the P=S bond adopts the axial or the equatorial orientation (Raevski, Vereshchagin, Khalitov

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32910 (78 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

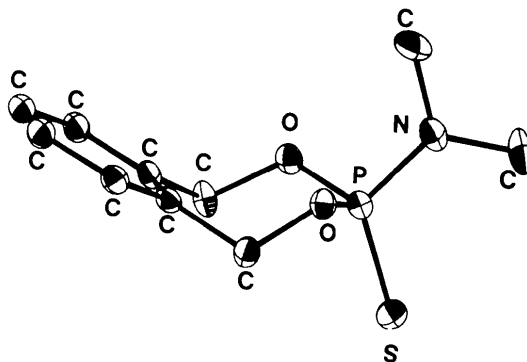


Fig. 2. 3-Thiono-3-*N*-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin.

Donskaya, Cherkasov & Ovchinnikov, 1972; Dutasta, Grand, Robert & Taieb, 1974; Guimaraes, Robert & Taieb, 1977) depending on the dielectric constant of the solvent.

In (II) and (IV), the exocyclic N and the atoms to which it is bonded form a planar system. The plane of the N—C bonds bisects the ring O—P—O angle and one N—C bond eclipses the P=S double bond. When such a stereochemistry exists around the P—N bond, the N is planar (Morris & Nordman, 1969; Brittain, Smith, Lee, Cohn & Schwendeman, 1971; Forti, Damiani & Favero, 1973; Camerman & Camerman,

1973; Garcia-Blanco & Perales, 1972; Sternglanz, Einspahr & Bugg, 1974; Clardy, Mosbo & Verkade, 1974; Martin & Robert, 1976; Grand, Robert & Filhol, 1977) otherwise it becomes pyramidal (Bullen, Stephens & Wade, 1969; Bullen & Dann, 1973; Mazhar-ul-Haque & Caughlan, 1976), as predicted from *ab initio* molecular-orbital calculations on the hypothetical H₂NPH₂ molecule where the N changes from trigonal planar to approximately tetrahedral by rotation around P—N (Cowley, Taylor, Whangbo & Wolfe, 1976). The two P—N—C angles around the planar N atom are quite different [125.5 and 120.0° in (II) and 124.7 and 119.4° in (IV)]. The larger values can be explained as being due to the eclipsed relationship of the P=S and N—C bonds.

Table 8. *Least-squares symmetry-plane equations for (I), (III) and (IV) and distances (Å) of the ring atoms to the symmetry planes*

2-Thiono-2,5,5-trimethyl-1,3,2-dioxaphosphorinane (I)							
$-0.6816X + 0.3855Y - 0.6220Z - 0.0732 = 0$							
O(1)	1.242	O(3)	-1.251	S	-0.007	C(7)	0.005
C(6)	1.244	C(4)	-1.244	P	0.003	C(5)	-0.002
C(7)	-0.002	C(8)	0.003				
3-Thiono-3-methyl-1,5-dihydro-2,4,3-benzodioxaphosphepin (III)							
$0.7517X - 0.0370Y - 0.6585Z - 2.1699 = 0$							
O(2)	-1.2740	O(4)	1.2519	C(11)	-1.4426	C(8)	-1.3141
C(1)	-1.5009	C(5)	1.4522	C(9)	-0.7675	C(10)	0.6127
C(7)	-0.7507	C(6)	0.6591				
3-Thiono-3-N-dimethylamino-1,5-dihydro-2,4,3-benzodioxaphosphepin (IV)							
$0.6609X - 0.6724Y - 0.3334Z + 11.0579 = 0$							
O(2)	1.240	O(4)	-1.257	C(8)	1.343	C(11)	-1.463
C(1)	1.448	C(5)	-1.549	C(9)	0.645	C(10)	-0.746
C(7)	0.653	C(6)	-0.763	C(13)	-0.0744	C(14)	0.125

Table 9. *Comparison of bond lengths and angles in six- and seven-membered rings*

	(I)	(II)	(III)	(IV)
Bond lengths (Å)				
P=S	1.924 (2)	1.919 (3)	1.925 (1)	1.923 (2)
P—C	1.771 (5)		1.771 (3)	
P—N		1.616 (8)		1.612 (5)
P—O	{ 1.581 (3) 1.582 (3)	{ 1.601 (4) 1.601 (4)	{ 1.595 (2) 1.587 (2)	{ 1.591 (4) 1.587 (4)
Bond angles (°)				
O—P—O	103.4 (1)	101.5 (5)	105.1 (9)	103.6 (2)
O—P—C	{ 102.9 (2) 103.4 (2)		{ 102.3 (1) 102.3 (1)	
O—P—N		{ 104.3 (2) 104.3 (2)		{ 104.2 (3) 102.4 (3)
O—P—S	{ 114.6 (1) 114.4 (1)	{ 114.6 (2) 114.6 (2)	{ 113.8 (1) 114.1 (1)	{ 114.2 (2) 114.7 (2)
S—P—C	116.6 (2)		117.6 (1)	
S—P—N		115.8 (3)		116.1
C—O—P	{ 116.0 (2) 115.7 (3)	116.00	{ 118.7 (1) 118.9 (2)	{ 119.4 (4) 120.4 (3)

It is interesting to compare the changes in bond angles and distances in going from a six- to a seven-membered ring in which the same chemical groups are attached to the P atom [*i.e.* (I) *vs* (III) and (II) *vs* (IV)]. The main values which may be compared are listed in Table 9. The bond lengths are equal within the limits of errors, and show no significant changes when a methyl group is replaced by a dimethylamino group.

Considering the bond angles around P, the most significant change in going from a six- to a seven-membered ring is an increase of about 2° of the O—P—O ring angle. Such a trend is also observed in 1,3,2-dioxaphospholanes and 1,3,2-dioxaphosphorinanes. In five-membered-ring phosphate esters (Steitz & Lipscomb, 1965; Chiu & Lipscomb, 1969; Newton, Cox & Bertrand, 1966; Swank, Caughlan, Ramirez, Madan & Smith, 1967; Boer, 1972; Newton & Campbell, 1974) the O—P—O ring angle is about 5° smaller than the normal average O—P—O angle of 103° in six-membered cyclic esters (Boer, 1972). The other bond angles around P are quite comparable. The internal P—O—C ring angle is smaller in the six- than in the corresponding seven-membered ring. Such a contraction of the P—O—C angle is also observed in phosphates where the P—O—C angle decreases upon constraint from *ca* 120° in acyclic systems (Calleri & Speakman, 1964; Pletcher, Sax & Yoo, 1972; Mazhar-ul-Haque & Caughlan, 1970) to *ca* 110° in five-membered rings (Newton & Campbell, 1974).

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