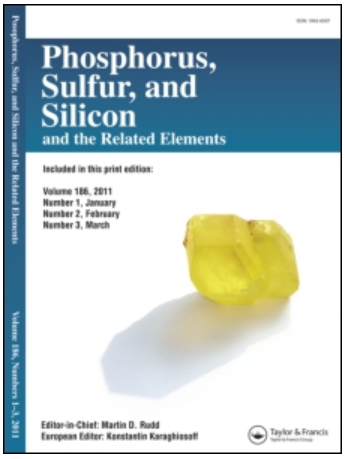

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STEREOCHEMISTRY OF ORGANOPHOSPHORUS CYCLIC COMPOUNDS XII. A Comparative Study of the Molecular Dimensions and Conformations of Thio-1,3-2-Dioxaphospholane Rings. Crystal and Molecular Structure of the Imidazolium Salt of 2-Hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane-2-sulphide

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STEREOCHEMISTRY OF ORGANOPHOSPHORUS CYCLIC COMPOUNDS XII.

A Comparative Study of the Molecular Dimensions and Conformations of Thio-1,3,2-Dioxaphospholane Rings. Crystal and Molecular Structure of the Imidazolium Salt of 2-Hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane-2-sulphide

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This work presents a comparative study of the geometry and conformation of the 1,3,2-dioxaphospholane ring and is part of a general investigation of the synthesis and geometrical isomerism of the cyclic five-membered phosphorus monothioacids. The following general conclusions may be drawn for the 1,3,2-dioxaphospholane derivatives.

1) the axial bond lengths P—S and P—O are dependent on the substitution pattern of the ring.

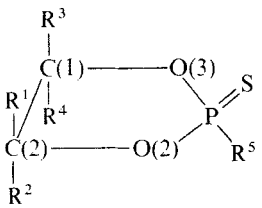
2) the conformation of the phospholane ring is influenced by intramolecular steric contacts.

3) hydrogen bonds from the dioxathiophospholanes contribute to the stabilization of the crystal lattices. Compound $C_7H_{13}N_2O_3PS$-*cis* (I) may be crystallized from a chloroform/benzene mixture.

Crystal Data: orthorhombic, a = 25.284(10), b = 7.119(3), c = 12.909(6) Å, Z = 8, space group $Pca2_1$, R = 0.078. The compound (I) contains two independent phospholane rings, the ring of one of which displays an envelope that of the second a half-chair conformation. The respective asymmetry parameters are $\Delta C_S^{C(1)} = 1.2$ (phosphorane ring A) and $\Delta C_2^P = 1.2°$ (phospholane ring B).

INTRODUCTION

This work summarises the present stand of information on penta-valent cyclic phosphorus derivatives of the type 1,3,2-dioxaphospholanes.



At present 17 structures of this type have been investigated. Table I gives a comparison of the structures with publication references. Crystal and refinement data for compounds (11)–(17) are summarized in Table II. A perspective view of the molecules with the numbering of the atoms is shown in Figures 1–7. The fundamental bond distances (Å) and bond angles for all structures are given in Table III. With the analyses of analogous bond distances and angles in the ring system it is possible to confirm that differing substituents give rise to significantly different bond distances and angles ($2–10\sigma$) and that the five-membered ring deforms (see discussion).

Comparing the structural data from the literature [Table III structure (1, 6, 8, 9, 10) solved after 1974 with a good degree of reliability] and the structures (11, 12, 14, 15, 16, 17) it is possible to confirm that the replacement of oxygen by sulphur leads to a slight increase in the bond distance $P—O_{ring}$ (3σ) and to a slight decrease in the bond angle $O_{ring}—P—O_{ring}$ (4σ) at phosphorus in the five membered ring. This is a result of the smaller electronegativity of sulfur in comparison to oxygen (S – 2.44, 0 – 3.50) and the larger Van der Waals radius of S (S – 1.85, 0 – 1.40). The bond distance

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TABLE I

Compounds (1)–(17)

Number and formula		References
1. $C_8H_{12}O_7P_2$	$R^1 = R^3 = Me$, $R^5 = C_4H_6O_4P$	14
2. $C_3H_7O_4P$	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = OMe$	15.16
3. $C_7H_{15}O_4P$	$R^1 = R^2 = R^3 = R^4 = Me$, $R^5 = OMe$	17
4. $C_2H_4O_3ClP$	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = Cl$	18
5. $C_{15}H_{15}O_4P$	A) $R^1 = R^3 = Ph$, $R^2 = R^4 = H$, $R^5 = OMe$	19
	B) $R^2 = R^4 = Ph$, $R^1 = R^3 = H$, $R^5 = OMe$	19
6. $C_5H_9O_4P$	$R^1 = R^3 = Me$, $R^5 = OMe$	20
7. $C_{18}H_{25}O_7N_2PS\ Na$	$R^1 + R^3 =$ ring, $R^2 = R^4 = H$, $R^5 = O^{\ominus}Na^{\oplus}\ C_6H_{15}$	21
8. $C_9H_{11}N_3O_7P\ Na$	$R^1 + R^3 =$ ring, $R^2 = R^4 = H$, $R^5 = O^{\ominus}Na^{\oplus}$	22
9. $C_9H_{11}N_3O_6PO^{\ominus}$	$R^1 + R^3 =$ ring, $R^2 = R^4 = H$, $R^5 = O^{\ominus}$	23
10. $C_{12}H_9O_5P$	$R^1 + R^3 =$ ring, $R^5 = O—O—Ph—OH$	24
11. $C_5H_9N_2O_3PS$	$R^1 = R^2 = R^3 = R^4 = H$, $R^5 = O^{\ominus}C_3H_5N_2^{\oplus}$	25
12. $C_6H_{11}N_2O_3PS$	$R^1 = R^2 = R^3 = H$, $R^4 = Me$, $R^5 = O^{\ominus}C_3H_5N_2^{\oplus}$	12 and Appendix 1
13. $C_7H_{13}N_2O_3PS$-dl	$R^1 = R^4 = Me$, $R^2 = R^3 = H$, $R^5 = O^{\ominus}C_3H_5N_2^{\oplus}$	13
14. $C_7H_{15}N_2O_4PS$-*trans*	$R^4 = R^2 = Me$, $R^1 = R^3 = H$, $R^5 = O^{\ominus}C_3H_{5\,2}^{\oplus}H_2O$	26
15. $C_7H_{13}N_2O_3PS$-*cis*	$R^1 = R^3 = Me$, $R^2 = R^4 = H$, $R^5 = O^{\ominus}C_3H_5N_2^{\oplus}$	
16. $C_9H_{17}N_2O_3PS$	$R^1 = R^2 = R^3$ $R^4 = Me$, $R^5 = OH \cdot C_3H_4N_2$	27
17. $C_{18}H_{26}NO_4PS$	$R^1 = R^3 = Ph$, $R^4 = R^2 = H$, $R^5 = O^{\ominus}N^{\oplus}(CH_3)_4 \cdot H_2O$	28

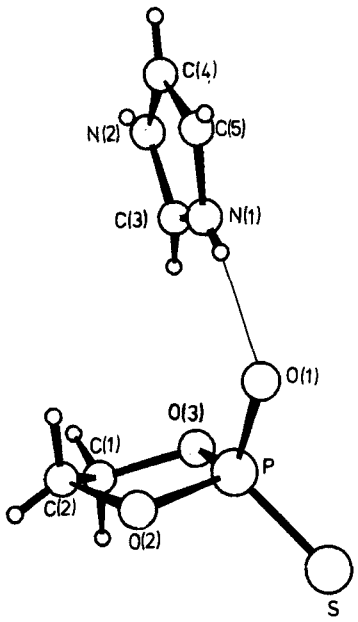

FIGURE 1 The molecule of $C_5H_9N_2O_3PS$-structure 11.

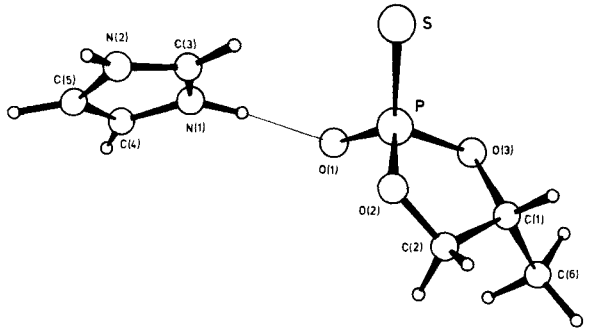

FIGURE 2 The molecule of $C_6H_{11}N_2O_3PS$-structure 12.

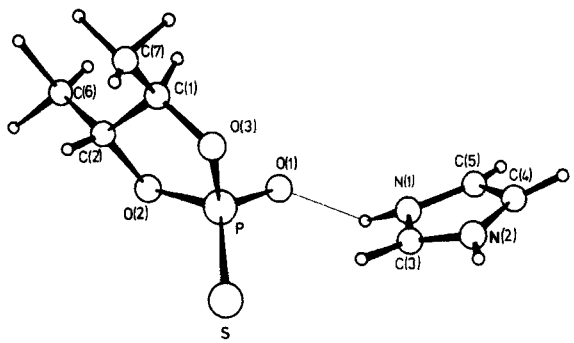

FIGURE 3 The molecule of $C_7H_{13}N_2O_3PS$-dl-structure 13.

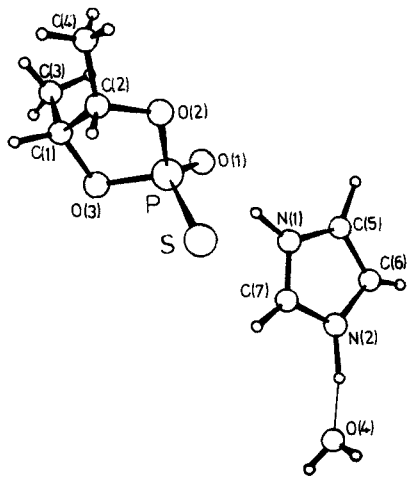

FIGURE 4 The molecule of $C_7H_{13}N_2O_3PS \cdot H_2O$-*trans*-structure 14.

TABLE II

Crystal and refinement data for compounds (11)–(17)

Compound	11	12	13	14	15A	15B	16	17
Stoichiometry	$C_5H_9N_2O_3PS$	$C_6H_{11}N_2O_3PS$	$C_7H_{13}N_2O_3PS$	$C_7H_{15}N_2O_4PS$	$C_7H_{13}N_2O_3PS$	$C_7H_{13}N_2O_3PS$	$C_9H_{17}N_2O_3PS$	$C_{18}H_{26}NO_4PS$
Conformation	C	C	C	C	C	D1	D1	D2
Config. subst.	—	*trans*	dl	*trans*	*cis*	*cis*	—	*cis*
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pca2_1$	$Pca2_1$	$P2_1/c$	$P2_1/c$
a (Å)	7.964(1)	7.818(5)	7.95(1)	7.239(1)	25.284(10)	25.284(10)	13.229(3)	19.298(4)
b (Å)	8.987(1)	9.736(5)	10.44(1)	13.044(2)	7.119(3)	7.119(3)	8.585(2)	9.848(1)
c (Å)	6.866(1)	6.958(5)	6.98(1)	6.802(1)	12.909(6)	12.909(6)	12.456(3)	10.856(2)
α (°)	106.63(9)	76.4(2)	98.0(5)	100.42(1)	90.0	90.0	90.0	90.0
β (°)	80.44(9)	98.2(2)	99.0(5)	73.33(1)	90.0	90.0	108.31(2)	96.44(4)
γ (°)	99.52(9)	97.2(2)	87.6(5)	98.64(1)	90.0	90.0	90.0	90.0
U (Å^3)	460.67	507.2	566.6	601.8	2323.5	2323.5	1343.0	2050.1
Z	2.0	2.0	2.0	2.0	8.0	8.0	4.0	4.0
M_r	208.18	222.21	236.21	254.27	236.21	236.21	264.21	383.44
D_c (g/cm^3)	1.509	1.467	1.392	1.410	1.358	1.358	1.314	1.249
Radiation	CuKα	MoKα	CuKα	CuKα	CuKα	CuKα	CuKα	MoKα
μ (cm^{-1})	44.01	3.97	36.30	34.80	35.44	35.44	31.10	2.12
2θ rang (°)	3.0–135.0	3.0–50.0	photo.	3.0–134.0	3.0–135.0	3.0–135.0	3.0–135.0	3.0–50.0
F rej. crite.	$<4.0\sigma(F)$	$<5.0\sigma(F)$		$<4.0\sigma(F)$	$<3.0\sigma(F)$	$<3.0\sigma(F)$	$<3.0\sigma(F)$	$<4.0\sigma(F)$
Numb. of refl.	1497	1380	1025	1551	1939	1939	2400	2732
R	0.060	0.094	0.135	0.041	0.078	0.078	0.081	0.056

TABLE III

Bond distances (Å) and bond angles (°) for compounds (1)–(17)

Number	P—O(S)	P—O(3)	P—O(2)	P—O	O(3)—C(1)	O(2)—C(2)	C(1)—C(2)	P—O(3)—C(1)	P—O(2)—C(2)	O(3)—C(1)—C(2)	O(2)—C(2)—C(1)	O(3)—P—O(2)
1A.	1.442(2)	1.579(2)	1.585(2)	1.595(2)	1.443(3)	1.424(3)	1.325(4)	108.7(2)	108.3(2)	111.0(3)	112.9(3)	98.5(1)
1B.	1.451(2)	1.575(2)	1.580(2)	1.605(2)	1.432(3)	1.432(3)	1.312(4)	108.5(2)	108.6(2)	112.3(3)	111.7(3)	98.1(1)
2.	1.45(1)	1.58(1)	1.59(1)	1.54(1)	1.42(2)	1.44(2)	1.56(2)	114.4(8)	112.4(8)	105.8(11)	108.5(12)	98.1(5)
3.	1.44(1)	1.57(1)	1.59(1)	1.56(1)	1.49(2)	1.50(1)	1.59(2)	112.3(8)	112.0(8)	102.0(1)	101.4(9)	98.4(5)
4.b	1.438	1.616	1.616	2.057[a]	1.488	1.488	1.547	106.4	106.4	108.2	108.2	104.7
5A.	1.443(5)	1.575(4)	1.584(4)	1.571(5)	1.470(8)	1.449(8)	1.551(9)	111.8(4)	109.3(4)	103.2(5)	103.5(5)	98.2(2)
5B.	1.445(5)	1.574(5)	1.599(5)	1.541(5)	1.481(8)	1.448(8)	1.576(9)	113.3(4)	111.8(4)	103.0(5)	104.9(5)	98.0(2)
6.	1.38(3)	1.57(2)	1.59(2)	1.53(2)	1.39(3)	1.36(4)	1.33(4)	106.0(11)	109.8(11)	115.3(16)	110.2(7)	98.5(6)
7.	1.946(10)	1.57(1)	1.61(1)	1.48(1)	1.50(1)	1.41(1)	1.55(1)	113.4(7)	115.4(7)	105.5(7)	107.3(7)	96.7(7)
8A.	1.471(2)	1.611(2)	1.616(2)	1.478(2)	1.466(7)	1.465(7)	1.542(7)	111.6(1)	112.1(1)	106.5(4)	107.5(4)	96.0(1)
8B.	1.468(2)	1.608(2)	1.616(2)	1.492(2)	1.461(7)	1.455(7)	1.567(7)	112.2(1)	111.0(1)	106.0(4)	106.7(4)	95.7(1)
9.	1.483(6)	1.597(6)	1.622(5)	1.496(6)	1.467(9)	1.418(10)	1.523(10)	112.5(6)	109.4(6)	103.5(6)	106.9(6)	96.4(6)
10.	1.448(3)	1.600(3)	1.601(3)	1.448(3)	1.406(4)	1.409(4)	1.375(5)	109.0(2)	108.9(2)			98.4(2)
11.	1.942(1)	1.603(2)	1.610(2)	1.497(2)	1.441(4)	1.454(4)	1.492(6)	109.9(2)	111.0(2)	105.2(3)	105.0(3)	96.6(1)
12.	1.939(2)	1.596(4)	1.618(6)	1.488(5)	1.517(9)	1.383(11)	1.495(12)	108.9(4)	112.0(6)	106.0(6)	107.9(8)	98.3(3)
13.	1.954(9)	1.62(1)	1.63(1)	1.52(3)	1.48(3)	1.52(3)	1.53(3)	110(1)	115(1)	109(2)	100(2)	95.7(8)
14.	1.958(1)	1.601(2)	1.608(2)	1.497(2)	1.461(3)	1.463(3)	1.522(4)	109.4(1)	111.4(1)	103.6(2)	103.2(2)	96.8(1)
15A.	1.936(3)	1.595(6)	1.603(5)	1.489(7)	1.448(11)	1.440(10)	1.532(13)	111.8(5)	110.6(5)	104.8(7)	103.0(6)	96.4(3)
15B.	1.935(4)	1.592(8)	1.600(5)	1.468(6)	1.462(12)	1.441(13)	1.557(15)	112.3(6)	111.2(6)	101.9(7)	104.3(8)	96.8(4)
16.	1.946(1)	1.603(3)	1.609(3)	1.502(3)	1.479(5)	1.491(5)	1.535(8)	111.0(6)	111.1(3)	102.9(4)	103.1(4)	96.8(1)
17.	1.941(1)	1.604(2)	1.620(2)	1.470(3)	1.451(4)	1.448(4)	1.551(4)	110.7(2)	113.4(2)	104.0(2)	104.8(2)	95.4(1)

[a] For Cl atom

[b] Elektronographi data.

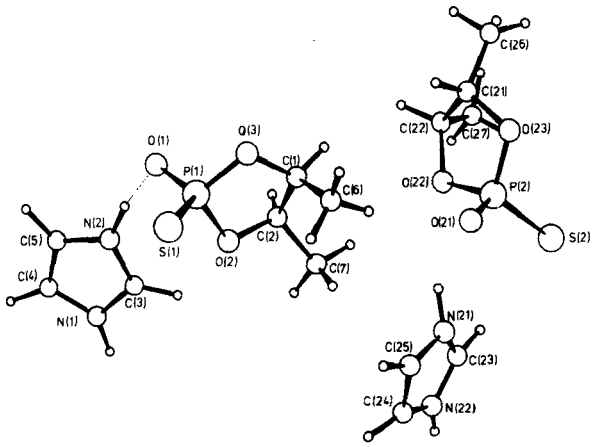

FIGURE 5 The molecule of $C_7H_{13}N_2O_3PS$-*cis*-structure 15A and 15B.

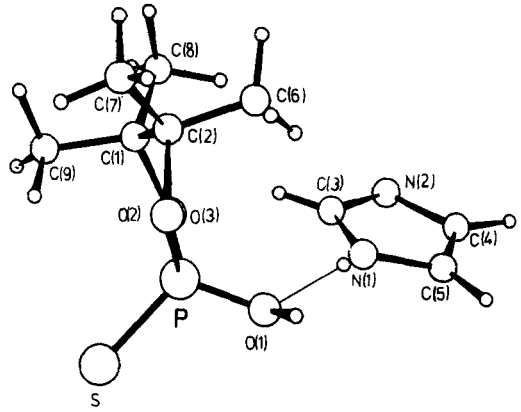

FIGURE 6 The molecule of $C_9H_{17}N_2O_3PS$-structure 16.

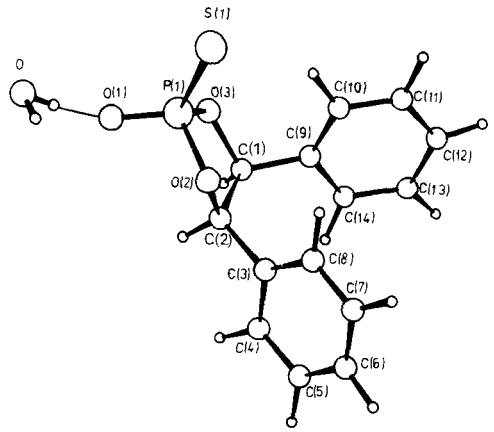

FIGURE 7 The molecule of $C_{18}H_{26}NO_4PS$-structure 17.

P—S has intermediate character between a single and a double bond. Using the method employed by Cruickshank[2] for oxygen, it is also possible to estimate the degree of π-character in the P—S bond.

The crystal and molecular structure investigations of compounds (11)–(17) have the objective of studying the geometry and conformation of the 1,3,2-dioxaphospholane ring and are part of a general study on the synthesis, geometrical isomerism and conformation of the cyclic five-membered phosphorus monothioacids. As a reference compound for examination of the geometry and conformation of these derivatives we may select 2-hydroxy-1,3,2-dioxaphospholan-2-thione (11), which has no ring substituents.

GEOMETRY

The replacement of an H atom by a methyl group (Figure 2 and structure 12) leads to a strong ring deformation, the bond length O(3)—C(1) increasing to 1.517 and O(2)—C(2) decreasing to 1.383 Å. The large deformation is associated with a difference of 3° in the bond angles PO(3)C(1) (108.9°) and PO(2)C(2) (112.0°) (standard deviation = 0.5°). The increase gives rise to a value for the ring bond angle at phosphorus of 98.3°. The atoms S and O are axially sited at angles of 53.4 and 62.8° to the equatorial dioxaphospholane ring [for structure (11) 50.9 and 64.7° respectively]. The CH_3 group is in the *trans*-position to the sulfur atom. The structure of (12) represents a decrease in the angle between oxygen and the plane and an increase in the angle between sulfur and the plane with regard to compound (11).

It is interesting to compare the geometries of the three isomers (13, 14, 15) which contain two methyl substituents. The structure (13), which has the two methyl substituents placed equatorially in the phospholane ring shows little difference with regard to the positions of the axial O and S atoms in comparison to structure (11).

For structure (14) which has the CH_3 groups in the *trans* position to sulfur (axially and equatorially to the phospholane ring), the angle of the best ring plane to the axial S increases by about 8° whereas the respective angle to the axial O decreases by about 9°. This must be the result of the short O(1) ··· H and C_{sub} ··· C_{sub} non-bonded distances.

Structure (15) has its two methyl groups in the *cis* relationship to sulfur in equatorial and axial

TABLE IV

Torsion bond angles and asymmetry parameters

Structure	P—O(2) (°)	P—O(3) (°)	O(2)—C(2) (°)	O(3)—C(1) (°)	C(1)—C(2) (°)	$\Delta C_s^{(x)}$ (°) x		$\Delta C_2^{(y)}$ (°) y	
1.			Planar						
2.	3.1	8.5	−12.3	−16.0	17.1	C(1)	2.8	P	4.6
3.	−12.2	−12.5	29.8	30.6	−35.3	C(1)	12.7	P	0.6
4.	—	—	—	—	—	—	—	—	—
5A.	1.3	22.5	−22.3	−36.9	35.7	C(1)	0.9	P	18.1
5B.	−5.8	−14.6	21.8	28.3	−29.8	C(1)	5.1	P	7.9
6.			Planar						
7.	−11.7	12.9	7.5	−9.5	1.2	P	1.7	C(2)	6.4
8A.	−21.2	25.6	10.7	−21.6	6.6	P	8.3	C(2)	2.9
8B.	−25.7	28.2	15.2	−21.7	4.0	P	4.8	C(2)	6.7
9.	4.0	−23.7	15.9	34.5	−30.7	C(1)	6.1	O(2)	9.8
10.			Planar						
11.	−4.4	−17.9	24.1	33.7	−35.2	C(1)	4.5	P	11.7
12.	−4.2	−12.9	18.4	25.4	−27.0	C(1)	4.1	P	7.9
13.	−6.6	−13.5	22.7	29.6	−31.0	C(1)	6.6	P	6.9
14.	−7.7	−18.0	29.1	36.3	−39.5	C(1)	8.2	P	8.9
15A.	−2.2	−21.4	23.0	35.9	−35.6	C(1)	1.2	P	16.4
15B.	12.0	12.9	−30.1	−31.4	36.8	C(1)	12.8	P	1.2
16.	−9.8	−15.7	30.3	34.5	−38.6	C(1)	10.7	P	5.1
17.	5.7	−25.7	14.1	36.0	−30.0	C(1)	9.2	O(3)	6.7

positions to phospholane ring. The unit-cell contains two independent molecules one with an envelope and one with a half-chair conformation. In the envelope conformer the best plane angles to the axial S and O(1) are similar to those in structure 11 (axial angle S − 50.1, I(1) − 65.7°). For the second molecule in the half-chair conformation these angles are 53.2 to the axial S and 60.8° to the axial O. In the structure with four methyl groups (16) the angles for the axial S and O(1) to the best ring plane are 55.8 and 58.9°. Of fundamental influence on the geometry and conformation of this molecule are the shorter intermolecular non-bonded distances between the methyl groups which are C(6) ··· C(7) = 2.51 Å, C(6) ··· C(8) = 2.90 Å, C(6) ··· C(9) = 3.91 Å,C(7) ··· C(8) = 3.40 Å, C(7) ··· C(9) = 2.97 Å and C(8) ··· C(9) = 2.49 Å respectively. The two *cis*-phenyl substituents (axial to the ring) in the structure (17) lead to short S ··· C_{sub} non-bonded distances. The angle of the ring plane to the axial sulfur undergoes a change to 47.6 (flattening) and to the axial oxygen an increase to 69.4°.

In recapitulation:

1) The axial bond lengths P—S and P—O are dependent on the substitution pattern of the ring;

2) The conformation of the phospholane ring is influenced by steric contacts.

Conformations of Phospholane Rings

For the purpose of an adequate description of the conformations of the 1,3,2-dioxaphospholanes, torsion bond angles and asymmetry parameters have been calculated.[8,9] For the structures (11–17) twist angles have also been calculated. The results for all structures are given in Table IV (for structures (1)–(10) these were calculated on the basis of the published positional parameters). With one exception, all structures in Table IV are distinctly different from the ideal envelope or half-chair conformations. The greatest deviation from the envelope conformation is observed for the structure (14) ($\Delta C_S^{C(1)} = 8.2°$). The characteristic torsion angle (ψ) for the envelope conformation is that for the bond situated opposite to the atom in the flap position. For the half-chair it is that for the bond between the two atoms displaced from the plane of the chair. These angles give the degree of twist between the envelope and half-chair conformations. The first characteristic torsion angle is 0 for the envelope and 48° for the half-chair conformation. The values of this angle for compounds (11)–(17) are given here:

	11	12	13	14	15 A	15 B	16	17
Ψ tors	4.4	4.2	6.6	7.7	2.2	36.8	38.6	36.0

TABLE V

Hydrogen bond lengths, angles and chain axes

	11	12	13	14	15 A	15 B	16	17
Average bond lengths	2.71	2.73	2.71	2.76	2.69	2.72	2.76	2.76
P(1) O(1) H(1)	123.5	120.1	131.8	128.4	117.5	117.8	121.6	122.4
P(1) O(1) H(2)	121.6	126.9	114.2	114.3	114.5	110.1	113.7	—
O(1) H(1) N(1)	167.4	168.7	119.3	173.5	163.4	176.8	160.8	158.4
O(1) H(2) N(2)	160.9	149.1	166.7	171.3	166.2	144.8	151.6	—
H(1) O(1) H(2)	114.9	113.0	109.4	104.8	127.1	129.5	110.5	—
N(1) O(1) N(2)	122.5	124.7	125.0	—	133.5	132.2	102.8	—
chain axes	a 6.866	a 6.958	a 6.980	a 6.802 and c 7.239	b 7.119 and c 12.909	b 7.119 and c 12.909	c 12.456	—

For 1,3,2-phospholane rings with R^1 and R^3 as methyl-substituents the characteristic conformation is predominantly envelope with one of the C atoms in the flap position. The bulky phenyl substituents in compound (17) lead to a conformation which shows predominantly half-chair character. Exchange of all H-atoms with methyl groups [structure (16)] leads to a marked half-chair conformation. These conclusions are in agreement with the results of other authors.

Hydrogen Bonds

Six of the seven structures (11)–(17) are imidazolium salts. The imidazolium cation has two nitrogens which may take part in hydrogen bonds with O(1) of the phospholane anion.

The hydrogen bonds in the dioxathiophospholanes contribute to the stabilisation of the crystal lattice. In alkaline solution these compounds are not stable. Crystallisation with one water molecule leads a further stabilisation with regard to moisture sensitivity [structures (14) and (17)]. The linking of imidazolium cations with the phospholane anions through hydrogen bonds creates chains along the shortest cell axis (Figures 8–14). Table V gives the hydrogen bond angles and chain axes.

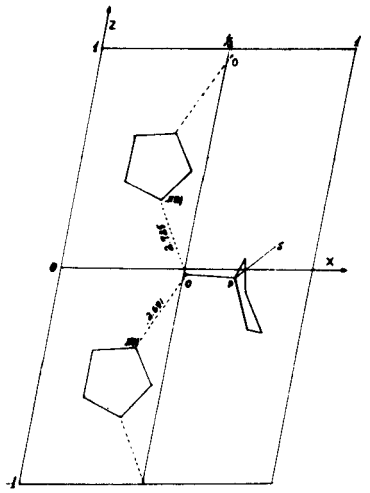

FIGURE 8 Projection of structure (11).

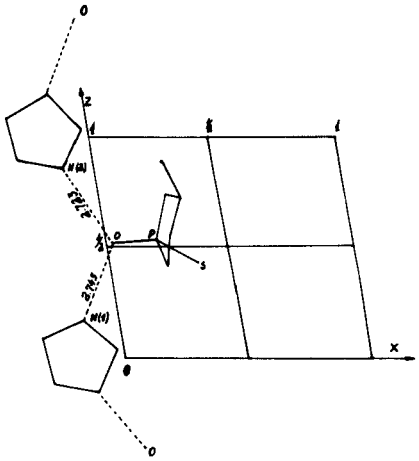

FIGURE 9 Projection of structure (12).

EXPERIMENTAL

Data for structure of the imidazolium salt of *cis*-2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane-2-sulphide $C_7H_{13}N_2O_3PS$. $C_7H_{13}N_2O_3PS$-*cis*-crystallizes from a chloroform/benzene mixture. The crystals are moisture sensitive. A plate-shaped crystal with approximate dimensions 0.42 × 0.40 × 0.10 mm was sealed into a Lindemann glass capillary tube. Intensity data were

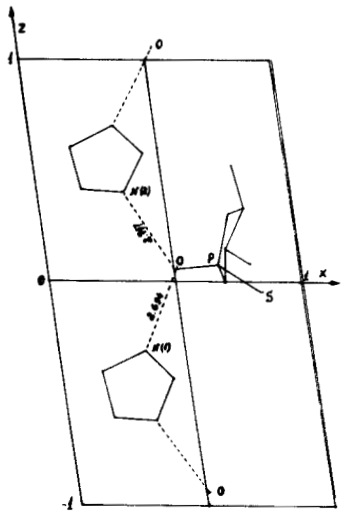

FIGURE 10 Projection of structure (13).

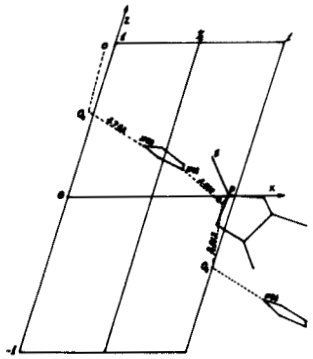

FIGURE 11 Projection of structure (14).

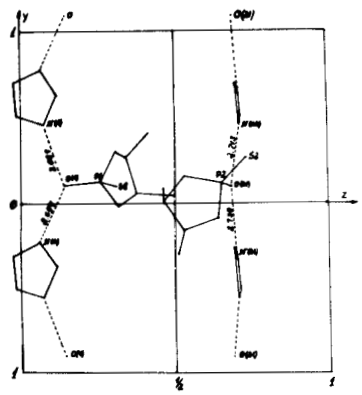

FIGURE 12 Projection of structure (15).

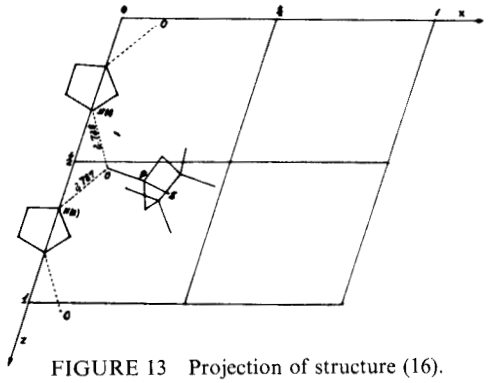

FIGURE 13 Projection of structure (16).

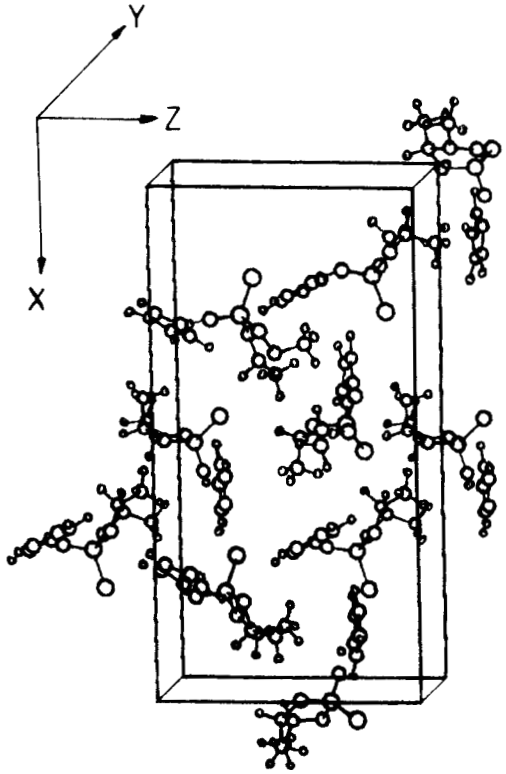

FIGURE 14 Stereoscopic packing of the crystal structures $C_7H_{13}N_2O_3PS$-*cis*.

collected on a Syntex $P2_1$ four-circle diffractometer by use of graphite monochromated Cu-Kα radiation.

Measurements were carried out in the θ–2θ scan mode for $3.0 \leqslant 2\theta \leqslant 135°$. A Lorentz polarization correction but no absorption [μ(CuKα) = 35.4 cm^{-1}] correction was applied. With the application of the acceptance criterion $F \geqslant 3.0\sigma$ (F), 1949 of the 2205 unique reflections measured were considered to be observed.

The structure was solved by direct methods (SHELX 76, G. M. Sheldrick, program TANG). Initial coordinates of 7 atoms P(1), S(1), O(1), O(2), P(2), O(21), O(22) were obtained from the E-map calculated from phases developed by weighted multisolution tangent refinement.

Several difference syntheses were carried out to find the positions of the other nonhydrogen atoms ($R = 0.17$). Refinement by blocked full-matrix least-squares with anisotropic temperature factors for all the non-hydrogen atoms converged to an R factor of $R = 0.104$. The methyl H atoms were refined as part of rigid groups, other H atoms were freely refined. Group isotropic temperature factors were assigned. Final temperature factors value of $R = 0.078$ of $R_w = (\Sigma w^{1/2} \Delta/\Sigma w^{1/2}|F_0|) = 0.082$. Weights were given by $w = k[\sigma(F_0) + 0.002 F_0^2]^{-1}$. Complex neutral-atom scattering factors were employed.[10,11]

DISCUSSION

The molecular structure of imidazolium salt *cis*-2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane-2-sulphide is depicted in Figures 5 and 14. The

TABLE VI

Least-squares planes for (15)

	Plane	Inclination angles	
i	P(1)O(2)O(3)C(1)C(2)	i/ii	60.7
ii	C(3)C(4)C(5)N(1)N(2)	i/iii	111.2
iii	P(2)O(22)O(23)C(21)C(22)	iii/iiii	78.1
iiii	C(23)C(24)C(25)N(21)N(22)	ii/iiii	64.3

TABLE VII

Positional parameters ($\times 10^4$) for the nonhydrogen atoms—structure 15A and 15B

	x/a	y/b	z/c
P(1)	2101(1)	1241(2)	2623(2)
S(1)	2827(1)	1014(3)	3085(3)
O(1)	2011(3)	1187(8)	1484(5)
O(2)	1827(2)	3074(7)	3104(4)
O(3)	1721(2)	−252(7)	3165(5)
C(1)	1338(3)	645(14)	3838(8)
C(2)	1295(3)	2660(13)	3430(8)
C(6)	1508(5)	368(18)	4930(9)
C(7)	1108(5)	4108(17)	4193(10)
N(2)	2108(3)	7727(8)	654(6)
C(4)	2319(5)	5176(12)	−191(8)
C(3)	1940(4)	6292(11)	1209(8)
N(1)	2084(3)	4675(9)	702(6)
C(5)	2331(5)	7033(11)	−225(7)
P(2)	−6(1)	1051(2)	6544(2)
S(2)	−444(1)	2697(3)	7373(3)
O(21)	547(2)	926(6)	6878(5)
O(22)	−10(3)	1583(9)	5346(6)
O(23)	−249(3)	−1012(7)	6419(5)
C(21)	−244(4)	−1602(14)	5351(9)
C(22)	−316(3)	251(15)	4727(8)
C(26)	−634(7)	−3129(21)	5151(12)
C(27)	−872(4)	909(22)	4643(11)
N(21)	970(3)	7438(8)	7044(6)
C(25)	1467(4)	6924(13)	7092(9)
N(22)	968(3)	4425(9)	7141(6)
C(23)	661(3)	5894(11)	7062(8)
C(24)	1476(4)	4978(14)	7146(10)

TABLE VIII

Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors ($Å^2 \times 10^3$)—structure 15A and 15B

	x/a	y/b	z/c	U
H(1)	943(3)	68(14)	3832(8)	107(26)
H(2)	996(3)	2730(13)	2833(8)	107(26)
H(61)	1183(5)	912(18)	5383(9)	133(19)
H(62)	1855(5)	1223(18)	5058(9)	133(19)
H(63)	1590(5)	−1061(18)	5162(9)	133(19)
H(71)	692(5)	3877(17)	4330(10)	133(19)
H(72)	1164(5)	5475(17)	3847(10)	133(19)
H(73)	1319(5)	4042(17)	4920(10)	133(19)
H(21)	2006(47)	9051(99)	902(98)	126(19)
H(41)	2470(5)	4231(12)	−776(8)	126(19)
H(31)	1727(4)	6374(11)	1934(8)	126(19)
H(11)	2027(45)	3321(72)	895(113)	126(19)
H(51)	2492(5)	7863(11)	−851(7)	126(19)
H(211)	117(4)	−2275(14)	5111(9)	94(23)
H(221)	−194(3)	−82(15)	3931(8)	94(23)
H(261)	−601(7)	−3337(21)	4325(12)	233(46)
H(262)	−1048(7)	−3104(21)	5367(12)	233(46)
H(263)	−439(7)	−4267(21)	5551(12)	233(46)
H(271)	−1163(4)	−9(22)	4295(11)	233(46)
H(272)	−867(4)	2231(22)	4233(11)	233(46)
H(273)	−975(4)	1151(22)	5445(11)	233(46)
H(21)′	824(29)	8745(51)	6965(72)	58(9)
H(251)	1846(16)	7486(99)	6900(63)	58(9)
H(22)′	868(29)	3232(68)	6760(58)	58(9)
H(231)	248(11)	5628(107)	6943(69)	58(9)
H(241)	1877(13)	4451(103)	7101(69)	58(9)

TABLE IX

Bond lengths (Å)—structure 15A and 15B

S(1)—P(1)	1.936(3)	O(1)—P(1)	1.489(7)
O(2)—P(1)	1.603(5)	O(3)—P(1)	1.595(6)
C(2)—O(2)	1.440(10)	C(1)—O(3)	1.448(11)
C(2)—C(1)	1.532(13)	C(6)—C(1)	1.488(16)
C(7)—C(2)	1.502(16)	C(3)—N(2)	1.318(11)
C(5)—N(2)	1.362(12)	N(1)—C(4)	1.345(12)
C(5)—C(4)	1.323(12)	N(1)—C(3)	1.374(11)
S(2)—P(2)	1.935(4)	O(21)—P(2)	1.468(6)
O(22)—P(2)	1.592(8)	O(23)—P(2)	1.600(5)
C(22)—O(22)	1.462(12)	C(21)—O(23)	1.441(13)
C(22)—C(21)	1.557(15)	C(26)—C(21)	1.490(19)
C(27)—C(22)	1.487(14)	C(25)—N(21)	1.309(11)
C(23)—N(21)	1.349(10)	C(24)—C(25)	1.387(13)
C(23)—N(22)	1.306(11)	C(24)—N(22)	1.344(13)
H(1)—C(1)	1.08(1)	H(2)— C(2)	1.08(1)
H(61)—C(6)	1.08(2)	H(62)—C(6)	1.08(2)
H(63)—C(6)	1.08(2)	H(71)—C(7)	1.08(2)
H(72)—C(7)	1.08(2)	H(73)—C(7)	1.08(2)
H(21)—N(2)	1.03(9)	H(41)—C(4)	1.08(1)
H(31)—C(3)	1.08(2)	H(11)—N(1)	1.01(6)
H(51)—C(5)	1.08(1)	H(211)—C(21)	1.08(2)
H(221)—C(22)	1.08(1)	H(261)—C(26)	1.08(2)
H(262)—C(26)	1.08(3)	H(263)—C(26)	1.08(2)
H(271)—C(27)	1.08(2)	H(272)—C(27)	1.08(2)
H(273)—C(27)	1.08(2)	H(21)′—N(21)	1.01(4)
H(251)—C(25)	1.07(5)	H(22)′—(22)	1.01(6)
H(231)—C(23)	1.07(3)	H(241)—C(24)	1.08(4)

TABLE X

Bond angles (°)—structure 15A and 15B

O(1)—P(1)—S(1)	116.6(4)	O(2)—P(1)—S(1)	111.0(2)
O(2)—P(1)—O(1)	109.7(3)	O(3)—P(1)—S(1)	112.3(3)
O(3)—P(1)—O(1)	108.9(4)	O(3)—P(1)—O(2)	96.4(3)
C(2)—O(2)—P(1)	110.6(5)	C(1)—O(3)—P(1)	111.8(5)
C(2)—C(1)—O(3)	104.8(7)	C(6)—C(1)—O(3)	108.5(8)
C(6)—C(1)—C(2)	118.0(9)	C(1)—C(2)—O(2)	103.0(6)
C(7)—C(2)—O(2)	110.2(7)	C(7)—C(2)—C(1)	116.1(9)
C(5)—N(2)—C(3)	107.8(7)	C(5)—C(4)—N(1)	107.7(8)
N(1)—C(3)—N(2)	107.7(8)	C(3)—N(1)—C(4)	107.7(7)
C(4)—C(5)—N(2)	108.9(8)	O(21)—P(2)—S(2)	114.9(3)
O(22)—P(2)—S(2)	113.0(3)	O(22)—P(2)—O(21)	107.7(4)
O(23)—P(2)—S(2)	113.1(3)	O(23)—P(2)—O(21)	109.8(3)
O(23)—P(2)—O(22)	96.8(4)	C(22)—O(22)—P(2)	112.3(6)
C(21)—O(23)—P(2)	111.2(6)	C(22)—C(21)—O(23)	104.3(8)
C(26)—C(21)—O(23)	111.9(9)	C(26)—C(21)—C(22)	116.9(10)
C(21)—C(22)—O(22)	101.9(7)	C(27)—C(22)—O(22)	109.7(9)
C(27)—C(22)—C(21)	114.5(9)	C(23)—N(21)—C(25)	109.1(7)
C(24)—C(25)—N(21)	107.3(8)	C(24)—N(22)—C(23)	109.5(7)
N(22)—C(23)—N(21)	108.0(8)	N(22)—C(24)—C(25)	106.0(8)

TABLE XI

Positional parameters ($\times 10^4$) for the nonhydrogen atoms—structure 12

	x/a	*y/b*	*z/c*
P	2084(2)	2581(2)	5273(2)
S	3578(3)	1529(2)	4282(3)
O(1)	218(6)	2032(6)	5208(6)
O(2)	2295(8)	4229(6)	4111(8)
O(3)	2707(6)	2794(6)	7479(7)
C(1)	3297(10)	4351(9)	7388(12)
C(2)	2528(12)	5138(12)	5404(13)
C(6)	2639(18)	4752(13)	9087(17)
C(3)	−317(9)	1608(8)	311(10)
C(5)	−3006(9)	1404(8)	−1103(11)
C(4)	−3042(10)	1230(9)	895(11)
N(1)	−1386(8)	1382(7)	1718(8)
N(2)	−1300(8)	1586(6)	−1381(8)

TABLE XII

Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors ($Å^2 \times 10^3$)—structure 12

	x/a	*y/b*	*z/c*	*U*
H(11)	4690(10)	4589(9)	7527(12)	184(31)
H(21)	3395(12)	6057(12)	4856(13)	184(31)
H(22)	1294(12)	5472(12)	5541(13)	184(31)
H(61)	3027(18)	5683(13)	9694(17)	140(23)
H(62)	3032(18)	3823(13)	10171(17)	140(23)
H(63)	1245(18)	4647(13)	8726(17)	140(23)
H(31)	1082(9)	1775(8)	525(10)	75(10)
H(51)	−4108(9)	1397(8)	−2233(11)	75(10)
H(41)	−4184(10)	1012(9)	1668(11)	75(10)
H(1)	−864(87)	1502(74)	3086(51)	75(10)
H(2)	−1168(95)	1816(74)	−2825(38)	75(10)

TABLE XIII

Bond lengths (Å)—structure 12

S—P	1.936(2)	O(1)—P	1.488(5)
O(2)—P	1.618(6)	O(3)—P	1.596(4)
C(2)—O(2)	1.383(11)	C(1)—O(3)	1.517(9)
C(2)—C(1)	1.495(12)	C(6)—C(1)	1.502(11)
N(1)—C(3)	1.339(8)	N(2)—C(3)	1.315(8)
C(4)—C(5)	1.365(9)	N(2)—C(5)	1.359(8)
N(1)—C(4)	1.344(9)		
H(11)—C(1)	1.08(0)	H(21)—C(2)	1.08(0)
H(22)—C(2)	1.08(0)	H(61)—C(6)	1.08(0)
H(62)—C(6)	1.08(0)	H(63)—C(6)	1.08(0)
H(31)—C(3)	1.08(0)	H(51)—C(5)	1.08(0)
H(41)—C(4)	1.08(0)	H(1)—N(1)	1.01(2)
H(2)—N(2)	0.99(2)		

compounds (15) contains two independent phospholane rings, the ring of one of which displays an envelope that of the second a half-chair conformation. The degrees of departure from the ideal symmetry of an envelope or half-chair conformation are small being. The torsion angles and asymmetry parameters[7,9] in the dioxaphospholane rings are given in Table IV. The characteristic angle ψ in the envelope conformation for the degree of twisting is 2.2°. The imidazole rings are planar (distances from the best least squares planes: C(3) − 0.017, C(4) − 0.003, C(5) − 0.008, N(1) 0.012, N(2) 0.016; C(23) − 0.008, C(24) − 0.007, C(25) 0.002, N(21) 0.004, N(22) 0.009 Å.)

TABLE XIV

Bond angles (°)—structure 12

O(1)—P—S	116.2(2)	O(2)—P—S	109.0(2)
O(2)—P—O(1)	110.4(3)	O(3)—P—S	114.4(2)
O(3)—P—O(1)	107.0(2)	O(3)—P—O(2)	98.3(3)
C(2)—O(2)—P	112.0(6)	C(1)—O(3)—P	108.9(4)
C(2)—C(1)—O(3)	106.0(6)	C(6)—C(1)—O(3)	107.6(7)
C(6)—C(1)—C(2)	112.4(9)	C(1)—C(2)—O(2)	107.9(8)
N(2)—C(3)—N(1)	106.7(6)	N(2)—C(5)—C(4)	105.8(6)
N(1)—C(4)—C(5)	107.0(6)	C(4)—N(1)—C(3)	109.8(5)
C(5)—N(2)—C(3)	110.5(5)		

In the crystal structure four hydrogen bonds have been detected:

$$O(1)\cdots H(11)-N(1)\ 2.69,\ O(1)\cdots H(21)'-N(2)'\ 2.70,\ O(21)\cdots H(21)'-N(21)'\ 2.71,\ O(21)\cdots H(22)-N(22)\ 2.73\ \text{Å}.$$

The angles between imidazolium ring planes and the planes of the phospholane rings are given in Table VI. Analogous angles for structures 11, 12, 13, 14, 16, 17 are in the range 56, 4–89.9°. Tables VII and VIII give the final positional parameters, Tables IX and X the bond lengths and angles, which are similar to those in other derivatives.

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Appendix 1

Further refinement of the structure imidazolium salt of 2-hydroxy-4-methyl-1,3,2,-dioxaphospholane-2-sulphide,[12] which was previously isotropically refined without H atoms, was by full-matrix least-squares with anisotropic temperature factors for all the non-hydrogen atoms and geometrically calculated H atoms with group isotropic temperature factors (rigid methyl groups). Final refinement values were $R = 0.094$ and

$$R_w = (\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_0|) = 0.097$$

(1584 reflections, 12.2, reflections/param.). Weights were given by $w = k[\sigma^2(F_0) + gF_0^2]^{-1}$ where k refined to 5.2013 and to $g = 0.000449$. Final results are given in Tables XI and XII (parameters), XIII and XIV (distances and angles), which refer to the atom numbering of Figure 2. The most interesting bond angle O(2) – P — O(3) is now 98.3° having altered by 0.8 with regard to the previous value of 97.5°. The remaining changes in molecular dimensions do not affect the previous chemical conclusions.

Appendix 2

In the structure of the imidazolium salt of *dl*-2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholane-2-sulphide ($C_7H_{13}N_2O_3PS$-structure 13)[13] the H atoms have now been geometrically established. The molecule is shown in Figure 3 and the new molecular dimensions are given in Table III.