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The Structure of the Imidazolium Salt of 2-Hydroxy-1,3,2-dioxaphospholane 2-Sulphide*

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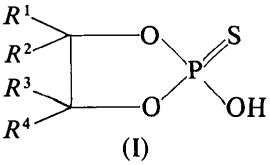
Abstract. $C_5H_9N_2O_3PS$, $M_r = 208{\cdot}18$, triclinic, $P\bar{1}$, $a = 7{\cdot}9636\,(8)$, $b = 8{\cdot}9868\,(9)$, $c = 6{\cdot}8663\,(7)$ Å, $\alpha = 106{\cdot}63\,(9)$, $\beta = 80{\cdot}44\,(9)$, $\gamma = 99{\cdot}52\,(9)^\circ$, $Z = 2$, $V = 460{\cdot}67$ Å^3, $D_m = 1{\cdot}499$, $D_c = 1{\cdot}509$ g cm^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}54178$ Å, μ(Cu $K\alpha$) $= 1{\cdot}87$ cm^{-1}, $F(000) = 216$. The crystal structure has been determined by direct methods and refined by full-matrix least-squares methods with 1497 independent reflections to a final R value of 0·0596. The dioxaphospholane ring has the open-envelope conformation with the C(1) atom in the flap position. The dioxaphospholane and imidazole rings are held together by hydrogen bonds.

Introduction. This work is a part of a general programme on the synthesis, geometrical isomerism and conformation of cyclic five-membered phosphorus monothioacids, 2-hydroxy-1,3,2-dioxaphospholane 2-sulphides (I). The general (Mikołajczyk, Witczak, Wieczorek, Bokij & Struchkov, 1976) and stereospecific (Mikołajczyk & Witczak, 1977) methods of synthesis of these thioacids as well as the X-ray structures of the imidazolium salts of *r*-2-hydroxy-4-methyl-1,3,2-dioxaphospholane 2-sulphide (I*b*) (Mikołajczyk *et al.*, 1976) and (±)-2-hydroxy-4,5-dimethyl-1.3.2-dioxaphospholane 2-sulphide (I*c*) (Wieczorek, Karolak-Wojciechowska, Groliński, Bartczak, Mikołajczyk & Witczak, 1976) were recently reported.



(I)

(*a*) $R^1 = R^2 = R^3 = R^4 = H$
(*b*) $R^1 = Me$, $R^2 = R^3 = R^4 = H$
(*c*) $R^1 = R^3 = Me$, $R^2 = R^4 = H$
(*d*) $R^1 = R^3 = Ph$, $R^2 = R^4 = H$
(*e*) $R^1 = R^2 = R^3 = R^4 = Me$

Now we report the X-ray analysis of the imidazolium salt of 2-hydroxy-1,3,2-dioxaphospholane 2-sulphide (I*a*). Knowledge of the ring conformation of the parent, unsubstituted thioacid (I*a*) is of great interest as far as the determination of the influence of substituents and configuration at P on the conformation of the 1,3,2-dioxaphospholane ring is concerned.

Approximate values of the unit-cell parameters were determined from oscillation and rotation photographs using Cu $K\alpha$ radiation. These parameters were redetermined on the automatic four-circle CAD-4 diffractometer using Cu $K\alpha$ radiation. 1497 reflections were measured of which 13 had $F_o < 4{\cdot}0\sigma|F_o|$ and these were not used in the refinement. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods with the multiple-solution program from the *SHELX* 76 (Sheldrick, 1976) system using 299 normalized structure factors with $E \geq 1{\cdot}2$. The E map calculated from the phase set with the highest figure of merit (1·05) revealed ten of the 12 non-hydrogen atoms. With these atoms in the model the discrepancy index $R = \sum (|F_o|$

Table 1. *Atomic parameters with e.s.d.'s in parentheses*

	x	y	z
P	0·7097 (1)	0·2642 (1)	−0·0376 (1)
S	0·8433 (1)	0·1685 (1)	0·0950 (1)
O(1)	0·5228 (3)	0·2034 (3)	−0·0340 (3)
O(2)	0·7862 (3)	0·2562 (2)	−0·2722 (3)
O(3)	0·7358 (4)	0·4512 (3)	0·0459 (4)
C(1)	0·7590 (5)	0·5209 (4)	−0·1228 (7)
C(12)	0·8528 (5)	0·4114 (4)	−0·2965 (6)
N(1)	0·3603 (4)	0·1706 (4)	−0·3603 (4)
N(2)	0·3540 (4)	0·1574 (3)	−0·6727 (3)
C(3)	0·4556 (4)	0·1509 (4)	−0·5342 (4)
C(4)	0·1897 (4)	0·1496 (4)	−0·5838 (5)
C(5)	0·1926 (4)	0·157 (4)	−0·3862 (5)
H(1)	0·387 (5)	0·174 (4)	0·725 (5)
H(2)	0·386 (5)	0·155 (4)	0·211 (6)
H(11)	0·644 (6)	0·514 (5)	−0·146 (7)
H(12)	0·811 (6)	0·613 (6)	−0·090 (6)
H(21)	0·986 (5)	0·417 (5)	−0·309 (5)
H(22)	0·837 (5)	0·406 (5)	−0·435 (6)
H(31)	0·477 (5)	0·171 (4)	0·426 (5)
H(41)	0·107 (5)	0·128 (4)	0·348 (6)
H(51)	0·111 (5)	0·167 (4)	0·709 (6)

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* Stereochemistry of Organophosphorus Cyclic Compounds. VII.

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *with e.s.d.'s in parentheses*

S–P	1·942 (1)	O(1)–P–O(2)	107·4 (1)
O(1)–P	1·497 (2)	O(1)–P–O(3)	110·6 (1)
O(2)–P	1·610 (2)	C(2)–O(2)–P	111·0 (2)
O(3)–P	1·603 (2)	C(1)–O(3)–P	109·9 (2)
C(2)–O(2)	1·454 (4)	C(2)–C(1)–O(3)	105·2 (3)
C(1)–O(3)	1·441 (4)	C(1)–C(2)–O(2)	105·0 (3)
C(1)–C(2)	1·492 (6)	C(5)–N(1)–C(3)	109·3 (3)
N(1)–C(3)	1·305 (4)	C(4)–N(2)–C(3)	109·0 (3)
N(1)–C(5)	1·357 (4)	N(2)–C(3)–N(1)	108·2 (3)
N(2)–C(3)	1·316 (4)	C(5)–C(4)–N(2)	107·0 (3)
N(2)–C(4)	1·348 (4)	C(4)–C(5)–N(1)	106·5 (3)
C(4)–C(5)	1·343 (4)	H(11)–C(1)–O(3)	100·8 (3)
C(1)–H(11)	0·948 (4)	H(11)–C(1)–C(2)	109·9 (4)
C(1)–H(12)	0·846 (4)	H(12)–C(1)–O(3)	110·4 (4)
C(2)–H(21)	1·042 (4)	H(12)–C(1)–C(2)	114·0 (4)
C(2)–H(22)	0·967 (4)	H(11)–C(1)–H(12)	115·2 (4)
N(1)–H(1)	0·642 (4)	H(21)–C(2)–O(2)	105·0 (3)
N(2)–H(2)	0·796 (2)	H(21)–C(2)–C(1)	120·4 (4)
C(3)–H(31)	0·964 (3)	H(22)–C(2)–O(2)	104·8 (3)
C(4)–H(41)	0·833 (3)	H(22)–C(2)–C(1)	118·9 (4)
C(5)–H(51)	0·842 (3)	H(22)–C(2)–H(21)	101·2 (3)
N(1)···N(2)	2·123	H(1)–N(1)–C(3)	126·4 (3)
N(1)···C(4)	2·163	H(1)–N(1)–C(5)	124·3 (3)
N(2)···C(5)	2·164	H(2)–N(2)–C(3)	124·5 (3)
C(3)···C(4)	2·169	H(2)–N(2)–C(4)	126·5 (3)
C(3)···C(5)	2·171	H(31)–C(3)–N(1)	131·7 (3)
		H(31)–C(3)–N(2)	119·8 (3)
O(2)–P–S	113·1 (1)	H(41)–C(4)–N(2)	122·2 (3)
O(3)–P–S	111·4 (1)	H(41)–C(4)–C(5)	129·9 (4)
O(1)–P–S	116·1 (1)	H(51)–C(5)–N(1)	124·7 (3)
O(3)–P–O(2)	96·6 (1)	H(51)–C(5)–C(4)	128·1 (4)

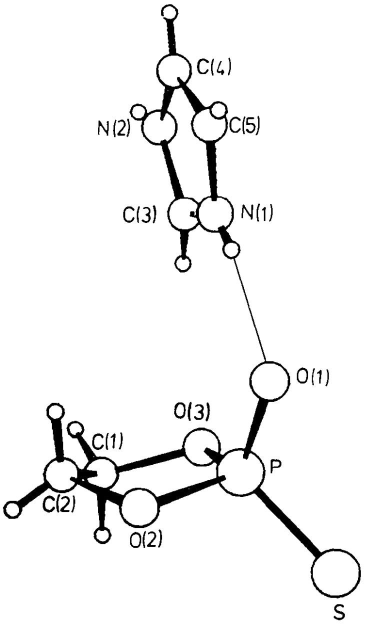

Fig. 1. The molecule of the imidazolium salt of 2-hydroxy-1,3,2-dioxaphospholane 2-sulphide.

— $|F_c|)/\sum|F_o|$ was 0·268. A Fourier map showed the positions of the remaining atoms.

Atomic positional and anisotropic thermal parameters were refined by a full-matrix least-squares method. A difference Fourier map showed the positions of the H atoms. The H positions were refined with isotropic temperature parameters. The final value of R is equal to 0·0596 with statistical weights $w = [\sigma^2F + 0{\cdot}0001F^2]^{-1}$.* All computations were performed with the *SHELX* 76 (Sheldrick, 1976) system on the ODRA-1305 computer.

The atomic parameters are given in Table 1. Interatomic distances and bond angles are given in Table 2. Fig. 1 shows the molecule projected along *b*.

Discussion. The five-membered phospholane ring is usually described as non-planar (Steiz & Lipscomb, 1965; Chiu & Lipscomb, 1969; Newton, Cox & Bertrand, 1966; Lee, Goodacre & Peake, 1970; Naumov, Siemashko, Zawialow, Tscherkhasov & Grishyna, 1973; Saenger & Eckstein, 1970; Swank, Caughlan, Ramirez & Madan, 1967; Coulter, 1973; Newton & Campbell, 1974; Mikołajczyk *et al.*, 1976; Andrianov, Kalinin & Struchkov, 1977; Wieczorek *et al.*, 1976).

In the imidazolium salt of 2-hydroxy-1,3,2-dioxaphospholane 2-sulphide (I*a*) the heterocyclic phospholane ring adopts the open-envelope conformation with C(1) at the flap position. This atom is 0·4917 Å above the plane passing through the atoms P, O(2), O(3) and C(2). The flap position for the C(1) atom clearly shows the dihedral angle between the plane through the atoms O(2), P, O(3) and the plane through O(2), C(1), O(3) of 17·93°, and that between the planes through O(2), P, O(3) and O(2), C(2), O(3) of 4·41°. As expected, the C(1) atom lies opposite the biggest angle C–O–P [C(2)–O(2)–P 111·0 (2)°]. The torsion angles in the dioxaphospholane ring are given in Fig. 2. Mirror symmetry dominates near the plane through C(1) and the P–O(2) bond with asym-

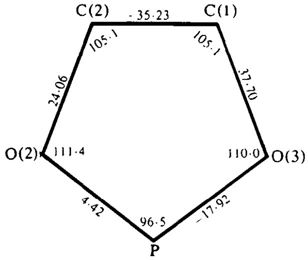

Fig. 2. Torsion angles in the dioxaphospholane ring.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33661 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

metry parameters (Duax & Norton, 1975) $\Delta C_S^{C(1)} = 4 \cdot 7°$ and $\Delta C_2^{P} = 13 \cdot 6°$.

As in compounds of the X=PO$_3$ type the X=P—O angles are larger than the O—P—O angles. The average value of the three O—P—O angles is 104·9° and S=P—O is 113·5°.

These values agree well with the angles observed by Newton & Campbell (1974) (104·9 and 113·7°, respectively).

The O(2)—P—O(3) ring angle of 96·6 (1)° is similar to the values found for other 1,3,2-dioxaphospholanes (Steiz & Lipscomb, 1965; Chiu & Lipscomb, 1969; Newton, Cox & Bertrand, 1966; Boer, 1972; Newton & Campbell, 1974; Mikołajczyk *et al.*, 1976; Wieczorek *et al.*, 1976). This angle is over 5° smaller than that found in six-membered cyclic compounds containing phosphorus: the 1,3,2-dioxaphosphorinanes (Cameron, Gałdecki & Karolak-Wojciechowska, 1976; Cameron & Karolak-Wojciechowska, 1977). The ring angles C(1)—O(3)—P of 109·9 (2)° and C(2)—O(2)—P of 111·0 (2)° are larger than the O(2)—C(2)—C(1) and O(3)—C(1)—C(2) angles which are 105·0 (3) and 105·2 (3)°, respectively.

Interatomic distances do not differ markedly from those normally observed. The thiophosphoryl bond P=S of 1·942 (1) Å lies within the range (1·85–1·96 Å) observed for substituted thionophosphates (Corbridge, 1974, p. 218). The thiophosphoryl S occupies a pseudo-axial position in the dioxaphospholane ring. Both C—O ring bonds C(1)—O(3) of 1·441 (4) Å and C(2)—O(2) of 1·454 (4) Å are longer than the aliphatic one of 1·43 Å. The bond lengths P—O(2) and P—O(3) are very similar, 1·610 (2) and 1·603 (2) Å, respectively. The bond length P—O(1) [1·497 (2) Å] is considerably shorter as a result of mesomerism in the monothiophosphate anion $[{>}P(=S)O^- \leftrightarrow {>}P(=O)S^-]$.

The imidazolium ring is planar. The maximum deviation from the mean plane of the ring is 0·0031 Å for the N(2) atom. The distances across the ring are given in Table 2. The angle between the imidazolium ring plane and the plane through the atoms P, O(2) and O(3) is 83·19°.

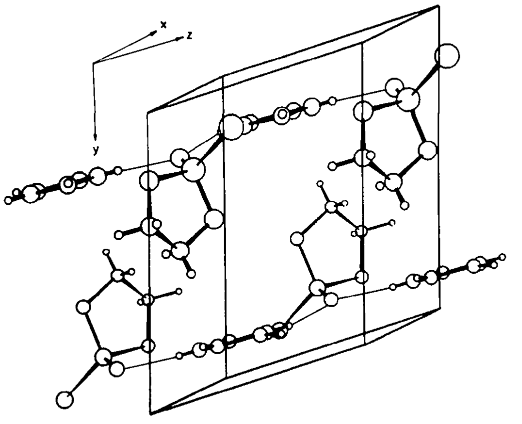

Fig. 3. The packing of the molecules in the unit cell.

In the crystal structure of the imidazolium salt of 2-hydroxy-1,3,2-dioxaphospholane 2-sulphide (I*a*) two hydrogen bonds have been detected: O(1)···H(1)—N(1) equal to 2·691 Å and O(1′)···H(2)—N(2) equal to 2·725 Å. Both hydrogen bonds have linear character (sums of the interatomic distances are 2·703 and 2·757 Å, respectively) and are strong, the O···N distance being short for this type of bond which is within the range 2·64–3·18 Å (Corbridge, 1974, p. 252). In both cases H atoms are more closely associated with the N atoms, which is in agreement with the rather short P—O(1) distance. The hydrogen bonds connect the phospholane ring with one imidazole ring by O(1)···N(1) contact and with the other by O(1)···N(2′). The —N(1)—H(1)···O(1)···H(2′)—N(2′) system forms chains along the *z* axis.

Besides the hydrogen bonds there are no other unusually short intermolecular contacts. The packing in the unit cell is shown in Fig. 3.

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