

large deviation from a normal sp^3 C—C distance is apparently caused by the eclipsed (within 4°) conformation of bulky C(2) and C(3) substituents, including a Cl atom and a dichloromethyl group at C(2) and two chloromethyl groups at C(3). Several other distances within the ring system are somewhat longer than normal, with no main contributing cause immediately apparent. The nonbonded C(1)—C(4) distance is only 2.25 Å (common for this type of ring system), suggesting the beginning of an approach to a bonding situation.

A projection of the unit-cell contents is shown in Fig. 2.

The authors thank Dr James N. Seiber (Department of Environmental Toxicology, University of California, Davis, California) for providing the sample and for financial support (KLS and PFL). This work was

supported by US Public Health Services grant ES00054 and NSF grant MPS73-05290.

References

- CASIDA, J. E., HOLMSTEAD, R. L., KHALIFA, S., PALMER, K. J. & WONG, R. Y. (1974). *Science*, **183**, 520–521.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 LANDRUM, P. F., POLLOCK, G. A., SEIBER, J. N., HOPE, H. & SWANSON, K. L. (1976). *Chemosphere*, **2**, 63–69.
 LAWTON, S. L. (1973). *TRACER II, a Fortran Lattice Transformation—Cell Reduction Program*. Accession No. 212, *J. Appl. Cryst.* **6**, 309–346.
 LONG, R. E. (1965). PhD Dissertation, Part III. UCLA.
 PALMER, K. J., WONG, R. Y., LUNDIN, R. E., KHALIDA, S. & CASIDA, J. E. (1975). *J. Am. Chem. Soc.* **97**, 408–413.
 SEIBER, J. N., LANDRUM, P. F., MADDEN, S. C., NUGENT, K. D. & WINTERLIN, W. L. (1975). *J. Chromatogr.* **114**, 361–368.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1978). **B34**, 3414–3417

The Imidazole Complex of 2-Hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-Sulphide*

BY M. W. WIECZOREK† AND J. KAROLAK-WOJCIECHOWSKA

Institute of General Chemistry, Technical University, 90-924, Łódź, Poland

M. MIKOŁAJCZYK AND M. WITCZAK

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 Łódź, Boczna 5, Poland

AND W. S. SHELDRIK

Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig-Stöckheim, Federal Republic of Germany

(Received 28 March 1978; accepted 26 June 1978)

Abstract. $C_6H_{13}O_3PS$. $C_3H_4N_2$, monoclinic, $P2_1/c$, $a = 13.229$ (3), $b = 8.585$ (2), $c = 12.456$ (3) Å, $\beta = 108.31$ (2)°, $Z = 4$, $D_m = 1.318$, $D_x = 1.314$ g cm $^{-3}$, $F(000) = 560$. The dioxaphospholane ring is in the half-chair conformation with C(1) and C(2) 0.373 and –0.236 Å from the O(2), P, O(3) plane. Asymmetry parameters $\Delta C_2^P = 5.1^\circ$ and $\Delta C_5^{C(2)} = 10.7^\circ$ are

observed. The imidazole and dioxaphospholane systems are linked into infinite chains through two strong hydrogen bonds O(1)⋯H(1)—N(1) 2.72 and O(1)—H(2)⋯N(2) 2.79 Å.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ diffractometer (Cu $K\alpha$, $\lambda = 1.54178$ Å). Intensity data were collected in the θ – 2θ mode ($3.0 \leq 2\theta \leq 135.0^\circ$) with graphite-monochromated Cu $K\alpha$ radiation. No absorption correction was applied [$\mu(\text{Cu } K\alpha) = 31.1$ cm $^{-1}$]. After application of the acceptance

* Stereochemistry of Organophosphorus Cyclic Compounds. VIII.

† To whom correspondence should be addressed at: Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig–Stöckheim, Federal Republic of Germany.

criterion $I \geq 2\sigma(I)$, 2400 unique reflexions were retained for the refinement. The structure was solved by the automatic centrosymmetric direct methods routine of *SHELX 76* (G. M. Sheldrick) and refined by a blocked full-matrix least-squares method with anisotropic temperature factors for all non-hydrogen atoms. The methyl H atoms, which were assigned a group isotropic temperature factor, were refined as part of rigid methyl groups. The remaining H atoms were allowed to refine freely with two group isotropic temperature factors. H(2) could not be unequivocally located in difference syntheses even with increased weighting of reflexions with small Bragg angles. Thus the diffraction data do not allow us to distinguish with complete certainty between the two possible formulations of (Ig), *i.e.* between an imidazole complex and an imidazolium salt. However, we did attempt to refine H(2), starting with geometrical parameters, in both of its conceivable positions for a near linear N(2)···O(1)

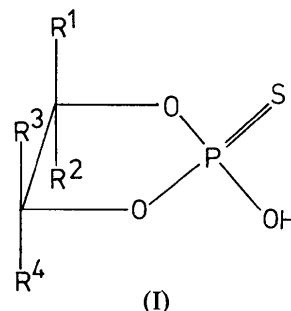
hydrogen bond, either directly bonded to O(1) or to N(2), with fixed O(1)—H(2) or N(2)—H(2) distances. This gave rise to respective temperature factors of 0.166 and $>0.50 \text{ \AA}^2$. It was therefore assumed for the final cycles that H(2) is directly bonded to O(1), *i.e.* that (Ig) is the imidazole complex. In analogous systems the X-ray evidence supports an imidazole complex for one case and the salt in two cases. There is no obvious rationalization. The O(1)—H(2) distance refined to 1.24 (7) Å [H(2)···N(2) = 1.73; O(1)···N(2) = 2.79 Å]. The terminal value of $R_w = (\sum w^{1/2} \Delta / \sum w^{1/2} F_o) = 0.093$ with $R = 0.081$. The weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where k and g refined to 1.2080 and 0.007220 respectively. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 1 and 2 give the final positional parameters, Tables 3 and 4 the bond lengths and angles.* Fig. 1 shows (I) in perspective with the numbering scheme, and Fig. 2 shows the unit-cell contents.

Table 1. Positional parameters ($\times 10^4$) for the non-hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>
P	2309 (1)	-923 (1)	5713 (1)
S	3088 (1)	1023 (1)	6126 (1)
O(1)	1119 (2)	-762 (3)	5267 (2)
O(3)	2663 (2)	-1967 (3)	4825 (2)
O(2)	2642 (2)	-2147 (3)	6743 (2)
C(2)	2921 (4)	-3688 (5)	6363 (4)
C(1)	3365 (3)	-3258 (5)	5402 (4)
C(6)	1867 (4)	-4627 (6)	5906 (5)
C(7)	3664 (6)	-4500 (8)	7379 (5)
C(8)	3291 (5)	-4515 (7)	4552 (5)
C(9)	4500 (4)	-2607 (8)	5846 (5)
C(5)	-1004 (4)	-2156 (5)	2604 (4)
N(2)	-3 (3)	-3110 (4)	1659 (3)
N(1)	59 (3)	-2052 (4)	3226 (3)
C(3)	632 (4)	-2611 (6)	2628 (4)
C(4)	-1019 (4)	-2846 (5)	1608 (4)

Table 2. Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(61)	2029 (4)	-5825 (6)	5750 (5)	117 (7)
H(62)	1260 (4)	-4169 (6)	5178 (5)	117 (7)
H(63)	1595 (4)	-4571 (6)	6637 (5)	117 (7)
H(71)	3887 (6)	-5606 (8)	7105 (5)	117 (7)
H(72)	3293 (6)	-4695 (8)	8025 (5)	117 (7)
H(73)	4366 (6)	-3790 (8)	7716 (5)	117 (7)
H(81)	3661 (5)	-5560 (7)	4983 (5)	117 (7)
H(82)	3630 (5)	-4235 (7)	3891 (5)	117 (7)
H(83)	2445 (5)	-4705 (7)	4185 (5)	117 (7)
H(91)	5010 (4)	-3559 (8)	6255 (5)	117 (7)
H(92)	4483 (4)	-1740 (8)	6468 (5)	117 (7)
H(93)	4803 (4)	-2093 (8)	5217 (5)	117 (7)
H(51)	-1675 (34)	-1828 (74)	2846 (53)	94 (9)
H(41)	-1688 (32)	-3151 (79)	907 (35)	94 (9)
H(31)	1376 (52)	-2688 (80)	2721 (59)	94 (9)
H(1)	249 (52)	-1819 (89)	3818 (60)	94 (9)
H(2)	677 (47)	-4108 (67)	1002 (56)	94 (9)



- (a) $R^1 = R^2 = R^3 = R^4 = \text{H}$
 (b) $R^1 = \text{Me}, R^2 = R^3 = R^4 = \text{H}$
 (c) $R^1 = R^3 = \text{Me}, R^2 = R^4 = \text{H cis}$
 (d) $R^2 = R^4 = \text{Me}, R^1 = R^3 = \text{H trans}$
 (e) $R^1 = R^4 = \text{Me}, R^2 = R^3 = \text{H} (\pm)$
 (f) $R^1 = R^3 = \text{Ph}, R^2 = R^4 = \text{H}$
 (g) $R^1 = R^2 = R^3 = R^4 = \text{Me}$

Discussion. This work is part of a general study on the synthesis, geometrical isomerism and conformation of the cyclic five-membered phosphorus monothioacids,

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33718 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (\AA)

S—P	1.946 (1)	O(1)—P	1.502 (3)
O(3)—P	1.603 (3)	O(2)—P	1.609 (3)
C(1)—O(3)	1.479 (5)	C(2)—O(2)	1.491 (5)
C(1)—C(2)	1.535 (8)	C(6)—C(2)	1.555 (7)
C(7)—C(2)	1.507 (7)	C(8)—C(1)	1.494 (8)
C(9)—C(1)	1.533 (7)	N(1)—C(5)	1.380 (6)
C(4)—C(5)	1.369 (8)	C(3)—N(2)	1.307 (6)
C(4)—N(2)	1.345 (7)	C(3)—N(1)	1.309 (8)

the 2-hydroxy-1,3,2-dioxaphospholane 2-sulphides (I). The general (Mikołajczyk, Witczak, Wieczorek, Bokiy & Struchkov, 1976) and stereospecific (Mikołajczyk & Witczak, 1977) methods of synthesis of these thioacids as well as the X-ray structures of the imidazole complex of (Ib) (Mikołajczyk, Witczak, Wieczorek, Bokiy & Struchkov, 1976) and the imidazolium salts of (Ia) (Wieczorak, Karolak-Wojciechowska, Mikołajczyk & Witczak, 1978) and (Ie) (Wieczorek, Karolak-Wojciechowska, Goliński, Bartczak, Mikołajczyk & Witczak, 1976) were recently reported. We report here the X-ray analysis of the imidazole complex (see *Introduction*) of 2-hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-sulphide (Ig).

The five-membered dioxaphospholane ring has been found to be non-planar in all previous investigations (Steitz & Lipscomb, 1965; Chiu & Lipscomb, 1969; Newton, Cox & Bertrand, 1966; Wieczorek, Karolak-

Wojciechowska, Goliński, Bartczak, Mikołajczyk & Witczak, 1976; Saenger & Eckstein, 1970; Mikołajczyk, Witczak, Wieczorek, Bokiy & Struchkov, 1976; Andrianov, Kalinin & Struchkov, 1977; Newton & Campbell, 1974; Bentrude & Han-Wan Tan, 1976). The dioxaphospholane ring in (Ig) displays a half-chair conformation [distances from the best least-squares plane: P 0·017, O(2) 0·121, C(2) -0·214, C(1) 0·230, O(3) -0·153 Å] with C(1) displaced more than C(2) from the plane defined by P, O(2) and O(3). This is evidenced by a comparison of the interplanar angles of 15·5 and 9·7° made by the plane defined by P, O(2) and O(3) with the planes involving O(2), C(1) and O(3), and O(2), C(2) and O(3) respectively. In contrast a symmetrical displacement of C(1) and C(2) was observed in an analogous tetramethylpinacol phosphate (Newton, Cox & Bertrand, 1966) for which the above interplanar angles were 12·2 and 12·1° respectively. These differences in conformation may be a result of the larger van der Waals radius of S in (Ig), which is involved in short intramolecular contacts with C(1) and C(9) [3·83 and 3·71 Å]. The torsion angles in the dioxaphospholane ring are given in Fig. 3. The corresponding asymmetry parameters (Duax & Norton, 1975; Altona, Geise & Romers, 1968) are $\Delta C_2^P = 5\cdot1^\circ$, $\Delta C_5^{C(2)} = 10\cdot7^\circ$ with $|\phi| = 25\cdot8^\circ$.

The O(2)-P-O(3) angle of 96·8° is similar to the values observed for other five-membered ring phosphates (see above; Ricci, Davis, Ramirez & Marecek, 1975; Boer, 1972; Coulter, 1973; Swank, Caughlan, Ramirez, Madan & Smith, 1967) and is 6·2° smaller than the average analogous endocyclic angle of 103·0° in six-membered rings. The C-O bond lengths of 1·491 (5) and 1·479 (5) Å in (Ig) are in

Table 4. Bond angles (°)

C(1)-P-S	115·2 (1)	O(3)-P-S	114·7 (1)
O(3)-P-O(1)	107·2 (1)	O(2)-P-S	111·1 (1)
O(2)-P-O(1)	110·4 (2)	O(2)-P-O(3)	96·8 (1)
C(1)-O(3)-P	111·0 (3)	C(2)-O(2)-P	111·1 (3)
C(1)-C(2)-O(2)	103·1 (3)	C(6)-C(2)-O(2)	107·1 (4)
C(6)-C(2)-C(1)	111·0 (4)	C(7)-C(2)-O(2)	107·8 (4)
C(7)-C(2)-C(1)	117·2 (5)	C(7)-C(2)-C(6)	109·9 (5)
C(2)-C(1)-O(3)	102·9 (4)	C(8)-C(1)-O(3)	107·8 (4)
C(8)-C(1)-C(2)	115·1 (4)	C(9)-C(1)-O(3)	107·2 (4)
C(9)-C(1)-C(2)	112·2 (4)	C(9)-C(1)-C(8)	110·9 (5)
C(4)-C(5)-N(1)	105·0 (5)	C(4)-N(2)-C(3)	109·4 (5)
C(3)-N(1)-C(5)	109·1 (4)	N(1)-C(3)-N(2)	109·1 (5)
N(2)-C(4)-C(5)	107·5 (4)		

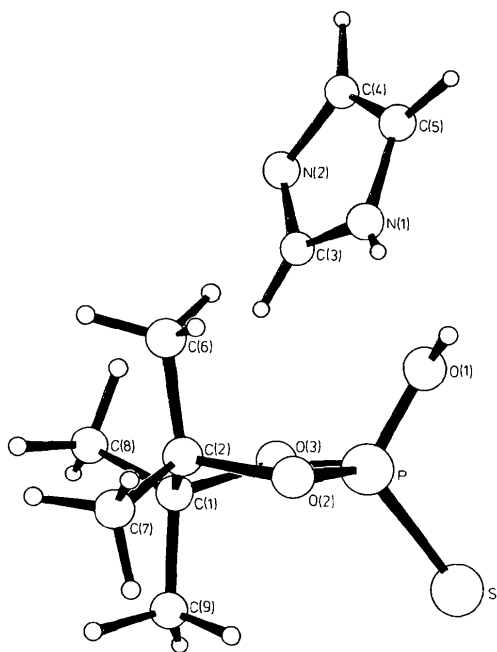


Fig. 1. (Ib) in perspective with numbering system.

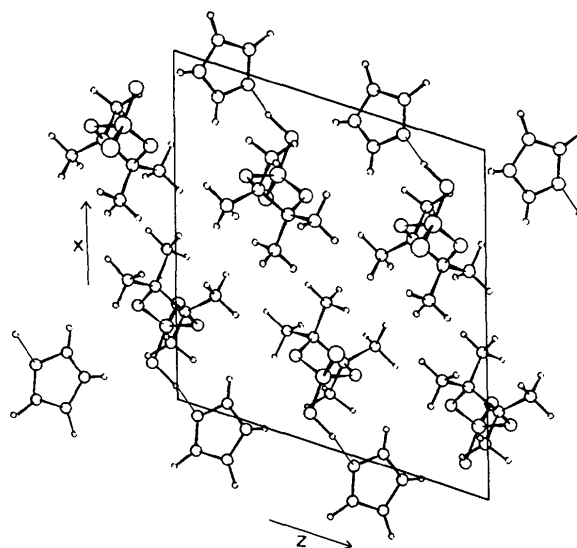


Fig. 2. The unit-cell contents of (Ib) perpendicular to [010].

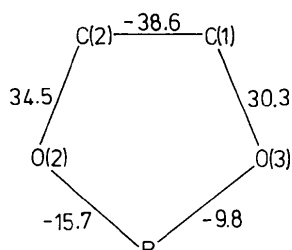


Fig. 3. Torsion angles in the dioxaphospholane ring (°).

accordance with recent cyclic phosphate structures which have revealed endocyclic C—O distances 0.03–0.04 Å longer than the aliphatic C—O single-bond distance of 1.43 Å. A value of about 120° has been observed for the P—O—C angles in a large number of acyclic phosphate esters (Newton & Campbell, 1974). In contrast to this are the P—O—C ring angles of 111.1 (3) and 111.0 (3)° in (I_g). This contraction of the P—O—C angles is one of the most significant differences between five-membered-ring phosphate esters and larger-ring or acyclic esters. The O(2)—C(2)—C(1) and O(3)—C(1)—C(2) angles of 103.1 (3) and 102.9 (4)° are much smaller than for undistorted tetrahedral coordination. The value of 1.946 (1) Å for the length of the P=S bond, which is axially sited at an angle of 55.9° to the equatorial dioxaphospholane ring, is within the range (1.85–1.96 Å) normally observed for substituted phosphates (Corbridge, 1974, p. 218). P—O(1) is 1.502 (3) Å at an angle of 57.8° to the ring.

The imidazole ring is planar [distances from the best least-squares plane: N(1) −0.008, N(2) −0.004, C(3) 0.007, C(4) −0.001, C(5) 0.005 Å]. Two strong hydrogen bonds are observed in the crystal lattice, O(1)⋯H(1)—N(1) 2.72 and O(1)—H(2)⋯N(2) 2.79 Å, which connect the dioxaphospholane and imidazole systems into chains along *c*. The O⋯N distances are short for such hydrogen bonds, which have been observed in the range 2.64–3.18 Å (Corbridge, 1974, p. 252).

References

- ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.
- ANDRIANOV, W. G., KALININ, A. J. & STRUCHKOV, YU. T. (1977). *Zh. Strukt. Khim.* **18**, 310–317.
- BENTRUDE, W. G. & HAN-WAN TAN (1976). *J. Am. Chem. Soc.* **98**, 1850–1859.
- BOER, F. P. (1972). *Acta Cryst.* **B28**, 1201–1204.
- CHIU, Y. H. & LIPSCOMB, W. N. (1969). *J. Am. Chem. Soc.* **91**, 4150–4155.
- CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*. Amsterdam: Elsevier.
- COULTER, C. L. (1973). *J. Am. Chem. Soc.* **95**, 570–575.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*, p. 18. New York: Plenum.
- MIKOŁAJCZYK, M. & WITCZAK, M. (1977). *J. Chem. Soc. Perkin Trans. 1*, pp. 2213–2222.
- MIKOŁAJCZYK, M., WITCZAK, M., WIECZOREK, M., BOKIY, N. G. & STRUCHKOV, YU. T. (1976). *J. Chem. Soc. Perkin Trans. 1*, pp. 371–377.
- NEWTON, M. G. & CAMPBELL, B. S. (1974). *J. Am. Chem. Soc.* **96**, 7790–7795.
- NEWTON, M. G., COX, J. R. JR & BERTRAND, J. A. (1966). *J. Am. Chem. Soc.* **88**, 1503–1506.
- RICCI, J. S., DAVIS, B. R. JR, RAMIREZ, F. & MARECEK, J. F. (1975). *J. Am. Chem. Soc.* **97**, 5457–5462.
- SAENGER, W. & ECKSTEIN, F. (1970). *J. Am. Chem. Soc.* **92**, 4712–4718.
- STEITZ, T. A. & LIPSCOMB, W. N. (1965). *J. Am. Chem. Soc.* **87**, 2488–2489.
- SWANK, D., CAUGHLAN, C. N., RAMIREZ, F., MADAN, O. P. & SMITH, C. P. (1967). *J. Am. Chem. Soc.* **89**, 6503–6506.
- WIECZOREK, M. W., KAROLAK-WOJCIECHOWSKA, J., GOLIŃSKI, B., BARTCZAK, T., MIKOŁAJCZYK, M. & WITCZAK, M. (1976). *Cryst. Struct. Commun.* **5**, 739–744.
- WIECZOREK, M. W., KAROLAK-WOJCIECHOWSKA, J., MIKOŁAJCZYK, M. & WITCZAK, M. (1978). *Acta Cryst.* **B34**, 3138–3140.

Acta Cryst. (1978). **B34**, 3417–3419

3-Aminomethyl-5-isoxazolol Monohydrate (Isomuscimol)

BY TAGE HONORÉ AND LOTTE BREHM

Royal Danish School of Pharmacy, Department of Chemistry BC, DK-2100 Copenhagen, Denmark

(Received 1 June 1978; accepted 26 June 1978)

Abstract. C₄H₆N₂O₂·H₂O, *M_r* = 132.12, m.p. 183.5°C, orthorhombic, *Pbca*, *a* = 16.426 (5), *b* = 10.205 (2), *c* = 7.568 (2) Å, *V* = 1268.6 Å³, *Z* = 8,

D_m (flotation) = 1.39, *D_x* = 1.383 g cm^{−3}. The structure was solved by direct methods and refined by least squares to *R* = 0.045. The isomuscimol molecules