

Tetramethylammonium Salt of *cis*-2-Hydroxy-4,5-diphenyl-1,3,2-dioxaphospholane 2-Sulphide Monohydrate*

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Abstract. C₁₈H₂₄NO₃PS·H₂O, monoclinic, $P2_1/c$, $a = 19.298$ (4), $b = 9.848$ (1), $c = 10.856$ (2) Å, $\beta = 96.46$ (4)°, $Z = 4$, $D_m = 1.23$, $D_c = 1.249$ Mg m⁻³, $F(000) = 816$. The dioxaphospholane ring adopts a conformation intermediate between half-chair and envelope with O(2) 0.158 and C(1) -0.364 Å from the P(1)O(3)C(2) plane. The respective asymmetry parameters are $\Delta C_2^{O(3)} = 6.7$ and $\Delta C_5^{C(1)} = 9.2$. The phenyl substituents make an angle of 49.0° with one another and respective angles of 68.6 and 76.0° with the best plane of the dioxaphospholane ring. The water of crystallization makes an O—H···O(1) hydrogen bond of length 2.76 Å.

Introduction. This work is part of a general study on the synthesis, geometrical isomerism and conformation of the cyclic five-membered phosphorus monothioacids, the 2-hydroxy-1,3,2-dioxaphospholane 2-sulphides (Mikołajczyk, Witczak, Wieczorek, Boki & Struchkov, 1976; Mikołajczyk & Witczak, 1977; Wieczorek, Karolak-Wojciechowska, Mikołajczyk & Witczak, 1978*a,b*; Wieczorek, Karolak-Wojciechowska, Goliński, Bartczak, Mikołajczyk & Witczak, 1976; Wieczorek, Karolak-Wojciechowska, Mikołajczyk, Witczak & Sheldrick, 1978). Here we report the structure of the tetramethylammonium salt of *cis*-2-hydroxy-4,5-diphenyl-1,3,2-dioxaphospholane 2-sulphide (I), which was determined in order to study the influence of two *cis* phenyl substituents at the endocyclic C atoms on the conformation of the dioxaphospholane ring.

Cell dimensions were determined by a least-squares fit to settings for 18 reflexions $\pm(hkl)$ on a Stoe Stadi-4 diffractometer (Mo $K\alpha$, $\lambda = 0.71069$ Å). Intensity data were collected in the θ - 2θ mode ($2\theta \leq 50.0^\circ$) with graphite-monochromated Mo $K\alpha$ radiation to yield 2732 unique reflexions [$I \geq 2.0\sigma(I)$]. The structure was solved by direct methods (SHELX 76, G. M. Sheldrick) and refined by a blocked full-matrix least-squares

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

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	6777 (1)	8851 (1)	7865 (1)
S(1)	6870 (1)	10306 (1)	9079 (1)
O(1)	6179 (2)	7929 (3)	7871 (3)
O(2)	7496 (1)	8022 (2)	7928 (2)
O(3)	6799 (1)	9396 (2)	6462 (2)
O	5556 (2)	7935 (5)	4899 (4)
C(1)	7639 (2)	7623 (3)	6696 (3)
C(2)	7369 (1)	8835 (3)	5864 (3)
C(3)	8387 (2)	7254 (3)	6718 (3)
C(4)	8902 (2)	7935 (4)	7457 (3)
C(5)	9594 (2)	7552 (5)	7463 (4)
C(6)	9773 (2)	6492 (4)	6732 (4)
C(7)	9268 (2)	5832 (4)	5980 (4)
C(8)	8578 (2)	6196 (3)	5978 (3)
C(9)	7883 (1)	9924 (3)	5649 (2)
C(10)	7970 (2)	11077 (3)	6343 (3)
C(11)	8459 (3)	12044 (4)	6108 (4)
C(12)	8863 (3)	11855 (5)	5169 (5)
C(13)	8791 (3)	10687 (5)	4464 (4)
C(14)	8303 (2)	9728 (4)	4691 (3)
C(15)	3998 (3)	7655 (5)	8456 (5)
C(16)	4452 (3)	8543 (9)	6617 (6)
C(17)	4408 (3)	9965 (5)	8434 (5)
C(18)	3322 (3)	9292 (6)	7232 (5)
N(1)	4049 (2)	8885 (3)	7638 (3)

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method with anisotropic temperature factors for all the non-hydrogen atoms. Difference syntheses revealed the positions of all the H atoms, which were allowed to refine freely under the bond-length constraint $d(C-H) = 1.08 \pm 0.02$ Å and with group isotropic temperature factors (Table 2). The terminal value of R' was 0.070 with R 0.056. Weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where k and g refined to 1.3572 and 0.04366 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 is a perspective view of the molecule and Fig. 2 shows the unit-cell contents.

Discussion. The dioxaphospholane ring in (I) displays a conformation intermediate between half-chair and envelope [distances from the best plane: P -0.096, O(2) 0.197, O(3) -0.020, C(1) -0.208, C(2) 0.127 Å]. The intermediate nature is illustrated by the atom distances from the least-squares planes through P(1), O(3) and C(2) [O(2) 0.158, C(1) -0.364 Å] and P(1), O(2), O(3) and C(2) [P(1) -0.031, O(2) 0.020, O(3) 0.035, C(1) -0.496, C(2) -0.025]. The degree of departure from the ideal symmetry of a half-chair or envelope conformation may be measured at the potential symmetry location by the asymmetry parameters ΔC_2 and ΔC_s (Altona, Geise & Romers, 1968). These functions compare related endocyclic torsion angles so that a respective value of zero will result if either a dyad axis (for the half-chair conformation) or a mirror plane (for the envelope conformation) is

Table 2. Hydrogen-atom positional parameters ($\times 10^4$)

	x	y	z
H(11)	7350 (15)	6856 (32)	6336 (27)
H(21)	7164 (14)	8438 (30)	5099 (29)
H(1)	5934 (39)	8268 (67)	5482 (66)
H(2)	5834 (25)	7702 (51)	4429 (45)
H(41)	8728 (23)	8830 (29)	7848 (40)
H(51)	9987 (18)	8135 (41)	7980 (38)
H(61)	10291 (13)	6117 (44)	6778 (41)
H(71)	9398 (21)	4975 (32)	5464 (36)
H(81)	8188 (18)	5595 (39)	5482 (37)
H(101)	7621 (17)	11314 (39)	6984 (30)
H(111)	8460 (21)	12994 (25)	6553 (34)
H(121)	9162 (17)	12699 (28)	4961 (35)
H(131)	9083 (18)	10642 (39)	3683 (26)
H(141)	8327 (21)	8757 (25)	4255 (34)
H(151)	4541 (13)	7472 (75)	8425 (60)
H(152)	3699 (31)	6741 (42)	8247 (64)
H(153)	3636 (28)	7670 (76)	9162 (47)
H(161)	4236 (32)	7735 (49)	6006 (51)
H(162)	4961 (19)	8247 (74)	7019 (60)
H(163)	4280 (35)	9432 (45)	6050 (55)
H(171)	4494 (37)	10640 (58)	7702 (47)
H(172)	4900 (20)	9471 (62)	8709 (61)
H(173)	4101 (32)	10059 (68)	9204 (45)
H(181)	3404 (35)	10082 (50)	6598 (50)
H(182)	3093 (34)	9395 (72)	8096 (38)
H(183)	3116 (32)	8323 (35)	6966 (63)

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33907 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å)

S(1)—P(1)	1.941 (1)	O(1)—P(1)	1.470 (3)
O(2)—P(1)	1.604 (2)	O(3)—P(1)	1.620 (2)
C(1)—O(2)	1.451 (4)	C(2)—O(3)	1.448 (4)
C(2)—C(1)	1.551 (4)	C(3)—C(1)	1.485 (4)
C(9)—C(2)	1.497 (4)	C(4)—C(3)	1.379 (4)
C(8)—C(3)	1.391 (4)	C(5)—C(4)	1.386 (5)
C(6)—C(5)	1.378 (6)	C(7)—C(6)	1.364 (6)
C(8)—C(7)	1.379 (5)	C(10)—C(9)	1.363 (4)
C(14)—C(9)	1.402 (5)	C(11)—C(10)	1.384 (6)
C(12)—C(11)	1.364 (8)	C(13)—C(12)	1.380 (7)
C(14)—C(13)	1.375 (6)	N(1)—C(15)	1.512 (6)
N(1)—C(16)	1.463 (7)	N(1)—C(17)	1.490 (6)
N(1)—C(18)	1.478 (6)		

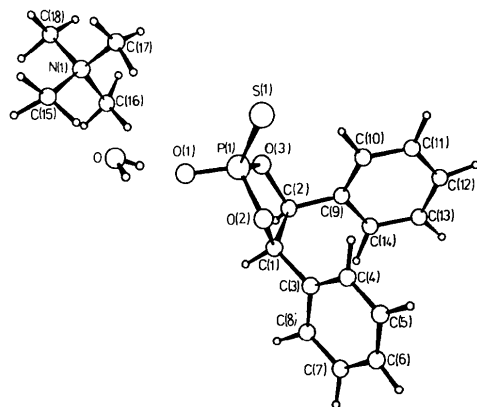


Fig. 1. Perspective view of the molecule with the numbering scheme.

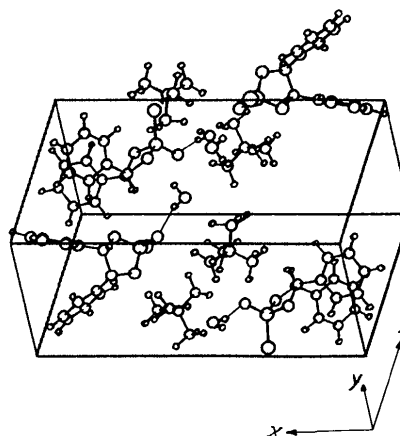


Fig. 2. The unit-cell contents.

present. For (I) the asymmetry parameters are $\Delta C_2^{O(3)} = 6.7$ and $\Delta C_s^{C(1)} = 9.2$ with a mean endocyclic torsion angle $|\phi|$ of 22.3° . The endocyclic torsion angles in the direction P(1)—O(2), O(2)—C(1) *etc.* are -25.7 , 36.0 , -30.0 , 14.1 and 5.7° .

An intermediate conformation has also been observed for other 1,3,2-dioxaphospholanes. The asymmetry parameters for the *trans*-2-hydroxy-4,5-dimethyl derivative (Wieczorek, Karolak-Wojciechowska, Mikołajczyk & Witczak, 1978*a*) are $\Delta C_2^{P(1)} = 9.0$ and $\Delta C_s^{C(1)} = 8.0^\circ$, and for the (\pm)-2-hydroxy-4,5-dimethyl derivative (Wieczorek, Karolak-Wojciechowska, Goliński, Bartczak, Mikołajczyk & Witczak, 1976) $\Delta C_2^{P(1)} = 6.9$ and $\Delta C_s^{C(1)} = 6.6^\circ$. For the 2-hydroxy-4,4,5,5-tetramethyl derivative (Wieczorek, Karolak-Wojciechowska, Mikołajczyk, Witczak & Sheldrick, 1978) $\Delta C_2^{P(1)} = 5.1$ and $\Delta C_s^{C(2)} = 10.7^\circ$ indicate a closer approach to the half-chair conformation. In contrast one of the two independent molecules with the analogous dioxaphospholane ring system in *cis*-2-methoxy-4,5-diphenyl-1,3,2-dioxaphospholane 2-oxide (Newton & Campbell, 1974) displays an almost perfect envelope conformation with $\Delta C_2^{P(1)} = 18.1$ and $\Delta C_s^{C(1)} = 0.9^\circ$. The second independent molecule in this derivative, however, displays an intermediate conformation with $\Delta C_2^{P(1)} = 7.9$ and $\Delta C_s^{C(1)} = 5.1^\circ$. The endocyclic O—P—O angle of $95.4(1)^\circ$ is 0.3 – 2.5° narrower than in other 1,3,2-dioxaphospholane 2-sulphides.

Steric contacts between the bulky phenyl substituents at C(1) and C(2) lead to a lengthening of the endocyclic C—C bond from $1.491(6)$ in the unsubstituted ring (Wieczorek, Karolak-Wojciechowska, Mikołajczyk & Witczak, 1978*b*) to $1.551(4)$ Å in (I). A similar endocyclic C—C bond distance of $1.567(10)$ Å is observed in *cis*-2-methoxy-4,5-diphenyl-1,3,2-dioxaphospholane 2-oxide. The axial P(1)=S(1) and P(1)—O(1) bonds make angles of 47.8 and 69.6° respectively with the best plane of the equatorial dioxaphospholane ring. (I) crystallizes with one water molecule which makes an O—H...O(1) hydrogen bond of length 2.76 Å.

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Table 4. Bond angles ($^\circ$)

O(1)—P(1)—S(1)	117.7 (1)	O(2)—P(1)—S(1)	109.5 (1)
O(2)—P(1)—O(1)	111.1 (2)	O(3)—P(1)—S(1)	112.6 (1)
O(3)—P(1)—O(1)	108.2 (2)	O(3)—P(1)—O(2)	95.4 (1)
C(1)—O(2)—P(1)	110.7 (2)	C(2)—O(3)—P(1)	113.4 (2)
C(2)—C(1)—O(2)	104.0 (2)	C(3)—C(1)—O(2)	109.7 (2)
C(3)—C(1)—C(2)	117.4 (3)	C(1)—C(2)—O(3)	104.8 (2)
C(9)—C(2)—O(3)	110.3 (2)	C(9)—C(2)—C(1)	117.1 (2)
C(4)—C(3)—C(1)	121.7 (3)	C(8)—C(3)—C(1)	119.6 (3)
C(8)—C(3)—C(4)	118.7 (3)	C(5)—C(4)—C(3)	120.1 (3)
C(6)—C(5)—C(4)	120.5 (4)	C(7)—C(6)—C(5)	119.8 (4)
C(8)—C(7)—C(6)	120.2 (4)	C(7)—C(8)—C(3)	120.8 (3)
C(10)—C(9)—C(2)	123.6 (3)	C(14)—C(9)—C(2)	117.8 (3)
C(14)—C(9)—C(10)	118.6 (3)	C(11)—C(10)—C(9)	121.0 (4)
C(12)—C(11)—C(10)	120.2 (4)	C(13)—C(12)—C(11)	119.8 (5)
C(14)—C(13)—C(12)	120.1 (4)	C(13)—C(14)—C(9)	120.2 (3)
C(16)—N(1)—C(15)	109.6 (4)	C(17)—N(1)—C(15)	106.8 (3)
C(17)—N(1)—C(16)	110.6 (4)	C(18)—N(1)—C(15)	105.7 (4)
C(18)—N(1)—C(16)	113.8 (4)	C(18)—N(1)—C(17)	110.0 (4)

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