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The Crystal and Molecular Structure of
Bis(5,5'-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) Sulphide

BY M. BUKOWSKA-STRZYŻEWSKA,* J. MICHALSKI,† B. MŁOTKOWSKA† AND J. SKOWERANDA

Institute of General Chemistry, Technical University, 36 Żwirki, 90–924 Łódź, Poland

The title compound, $C_{10}H_{20}O_6P_2S$, crystallizes in the orthorhombic system, $a = 18.66$, $b = 9.25$, $c = 9.05$ Å (with an e.s.d. of ~ 0.01 Å); space group $Pbcn$; $Z = 4$. The structure was solved by Fourier methods and refined by least-squares methods with anisotropic temperature factors to give an R value of 0.091 for 609 observed reflexions. The symmetry of the bicyclic molecules is C_2. The dioxaphosphorinane rings have partially flattened chair conformations with the double-bonded oxygen in equatorial and the linkage sulphur in axial positions. The P–S bond lengths are 2.105 (5) Å, the bond angle P–S–P is 102.2 (2)°. The bond angles around phosphorus range from 102.4 (4) to 115.2 (5)°. Some bond distances are: P=O 1.449 (11), P–O 1.565 (9) and 1.563 (9); C–O distances range from 1.470 (17) to 1.502 (17) and C–C from 1.514 (19) to 1.580 (17) Å. The structural results are compared with those for related compounds.

Introduction

Ring systems containing phosphorus occur in nucleic acids and in a number of biological reactions. The chemical reactivity, conformation and crystal structures of these compounds have recently become the subjects of intensive studies (Katritzky, Nesbit, Michalski, Tulimowski & Zwierzak, 1970; Edmundson & Mitchell, 1970).

The condensed 1,3,2-dioxaphosphorinanes have been obtained for the first time during the last ten years (Edmundson, 1965; Michalski, Mikołajczyk, Młotkowska & Zwierzak, 1967). Their crystal and molecular structures have not been investigated. The present study is a three-dimensional single-crystal X-ray diffraction analysis of bis(5,5'-dimethyl-2-oxo-1,3,2-

dioxaphosphorinanyl) sulphide. We were interested in considering the effect of linking the two dioxaphosphorinanyl rings by a sulphur atom on their conformation. This linkage through the sulphur atom should also have an effect on the symmetry of the molecule and may influence the bond lengths and bond angles in the P–S–P group of the bicyclic thiophosphate.

Experimental

The crystals used for X-ray diffraction were crystallized from a mixture of benzene and chloroform at room temperature. The colourless transparent crystals are plate-shaped (plate face is the (100) plane).

For data collection, crystals having approximate dimensions $0.2 \times 0.25 \times 0.2$ mm were mounted on the goniometer head and aligned along **b** and **c**.

The cell dimensions were determined from Weissenberg photographs taken with copper radiation. The unit-cell parameters and their e.s.d.'s were refined by

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* Author to whom correspondence should be addressed.
† Present address: Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90–362 Łódź.

the least-squares method for the spacings of 12 large-angle reflexions. The density was determined by flotation.

Crystal data

Formula: $C_{10}H_{20}O_6P_2S$; crystal system: orthorhombic; $a = 18\cdot66$ (2), $b = 9\cdot25$ (1), $c = 9\cdot05$ (1) Å, $V = 1562\cdot1$ Å³; $M = 330\cdot3$; $D_x = 1\cdot40$, $D_m = 1\cdot42$ g cm⁻³, $Z = 4$; $F(000) = 616$; $\lambda(\text{Cu } K\alpha) = 1\cdot5418$ Å; space group: $Pbcn$ (No. 60); $\mu(\text{Cu } K\alpha) = 40\cdot1$ cm⁻¹.

The space group is $Pbcn$ (from the systematic absences). Equi-inclination Weissenberg film data were taken with the multiple-film technique on the 0 to 3 and 0 to 8 layers around the b and c crystal axes respectively.

The intensities were visually estimated with a calibrated intensity scale. In total 1307 reflexions were collected. As the diameter of the crystals used did not exceed 0·25 mm ($\mu R = 0\cdot4$–$0\cdot5$) no absorption correction was made. The intensities were brought to a common scale by multiple-film and interlayer scaling after application of the Lp corrections.

Determination of the structure

The two-dimensional Patterson syntheses were computed and the peaks due to the intramolecular non-bonded P–P atoms and bonded P–S atoms were determined. The three-dimensional Fourier synthesis located the remaining atoms. The structure was refined by full-matrix least-squares calculations. In the final stage of the refinement a Cruickshank weighting scheme with $w = (10\cdot0 + F_o + 0\cdot002F_o^2)^{-1}$ was used and all the atoms were allowed to vibrate anisotropically. The final value of R for all observed reflexions was 0·091. Hydrogen atoms were ignored. Form factors for neutral atoms were taken from Doyle & Turner (1968).

The final positional ($\times 10^4$) and thermal ($\times 10^4$) parameters with estimated standard deviations are listed in Table 1.* The structure of the title compound was determined with the programs of the X-RAY

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31757 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

70 system (Stewart, Kundell & Baldwin, 1970) on an IBM-360 computer.

Molecular geometry and packing

A view of the molecule is shown in Fig. 1. Intramolecular bond lengths and valency angles are shown in Tables 2 and 3 and in Fig. 2.
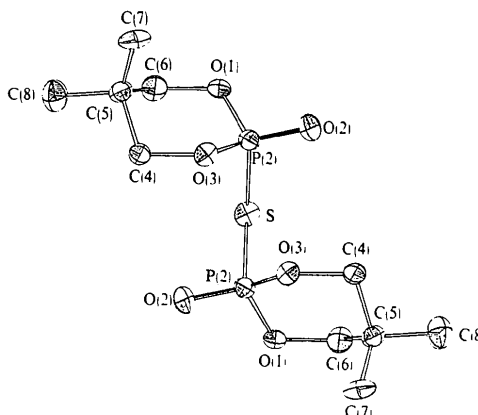

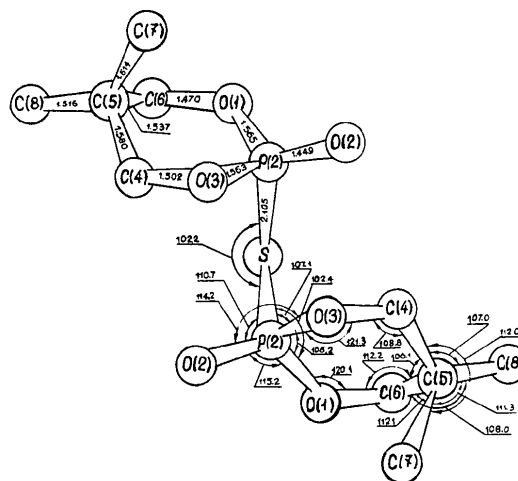Fig. 1. Atom numbering of bis-(5,5'dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulphide.

Fig. 2. Intramolecular bond lengths (Å) and angles (°).

Table 1. *Final atomic positions and temperature factors* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	0	3998 (5)	2500	605 (23)	483 (24)	680 (33)	0	−51 (33)	0
P(2)	878 (1)	2570 (4)	2507 (5)	428 (14)	564 (18)	492 (21)	−13 (13)	35 (19)	−62 (22)
O(1)	1470 (4)	3478 (10)	3306 (10)	373 (42)	718 (57)	579 (59)	−130 (42)	24 (39)	3 (49)
O(2)	1053 (5)	2117 (12)	1017 (11)	712 (61)	1092 (89)	512 (69)	92 (58)	95 (51)	−164 (63)
O(3)	685 (4)	1301 (8)	3576 (10)	570 (48)	395 (46)	572 (63)	−8 (40)	−57 (42)	−46 (46)
C(4)	657 (6)	1519 (15)	5220 (16)	460 (59)	609 (79)	507 (88)	−180 (61)	12 (59)	89 (66)
C(5)	1385 (6)	2226 (14)	5743 (15)	466 (62)	619 (78)	578 (97)	−41 (64)	−88 (65)	62 (71)
C(6)	1445 (7)	3673 (16)	4917 (15)	675 (90)	642 (93)	694 (113)	−288 (78)	−27 (74)	9 (78)
C(7)	2021 (6)	1251 (19)	5451 (21)	394 (62)	923 (120)	1127 (131)	117 (76)	−164 (77)	−22 (112)
C(8)	1308 (9)	2551 (19)	7377 (20)	1063 (119)	878 (111)	680 (114)	−61 (104)	32 (108)	−122 (96)

The molecule has C_2 symmetry. The P(2)–S–P'(2) angle is 102·2°. The P(2)–S distances (2·105 Å) correspond to the single-bonded atoms. The conforma-

Table 2. *Intramolecular bond lengths* (Å) *with e.s.d.'s in parentheses*

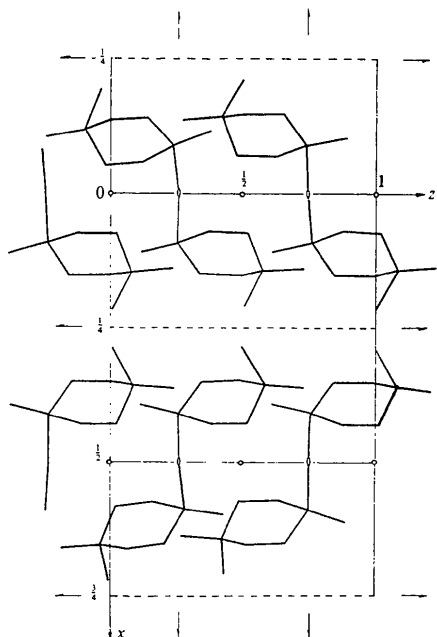|			
P(2)–S	2·105 (5)	O(3)–C(4)	1·502 (17)
P(2)–O(1)	1·565 (9)	C(4)–C(5)	1·580 (17)
P(2)–O(2)	1·449 (11)	C(6)–C(5)	1·537 (20)
P(2)–O(3)	1·563 (9)	C(5)–C(7)	1·514 (19)
O(1)–C(6)	1·470 (17)	C(5)–C(8)	1·516 (23)

Fig. 3. The packing of molecules in the crystal, projected along the *b* axis.

Table 3. *Valency angles* (°) *with e.s.d.'s in parentheses*

P(2)–S——P'(2)	102·2 (2)	O(1)–C(6)–C(5)	112·2 (11)
O(1)–P(2)–O(3)	106·2 (5)	O(3)–C(4)–C(5)	108·8 (10)
O(1)–P(2)–O(2)	115·2 (5)	C(4)–C(5)–C(6)	106·1 (10)
O(2)–P(2)–S	110·7 (4)	C(4)–C(5)–C(8)	107·0 (11)
O(3)–P(2)–S	107·1 (3)	C(8)–C(5)–C(7)	111·3 (13)
O(3)–P(2)–O(2)	114·2 (6)	C(7)–C(5)–C(6)	112·1 (11)
O(1)–P(2)–S	102·4 (4)	C(8)–C(5)–C(6)	108·0 (12)
P(2)–O(1)–C(6)	120·1 (8)	C(7)–C(5)–C(4)	112·0 (11)
P(2)–O(3)–C(4)	121·3 (7)		

tion of the rings is distorted chair with the double-bonded oxygen atom in equatorial position and the linkage sulphur atom in axial position. The P(2)–O(1) and P(2)–O(3) distances differ only slightly, the two esterified oxygens being 1·565 and 1·563 Å from the phosphorus atoms, while the shorter P(2)–O(2) distance is 1·449 Å. The C–O and C–C distances are normal, as in some other 1,3,2-dioxaphosphorinane rings (Beineke, 1969; Haque, Caughlan, Hargis & Bentrude, 1970; Rodgers, White & Verkade, 1971; Silver & Rudman, 1972; Cameron, Karolak-Wojcie-chowska & Zwierzak, 1976; Cameron, Gałdecki, & Karolak-Wojciechowska, 1976; Grand & Robert, 1975; Grand, Martin, Robert & Tordjman, 1975). The P–O–C angles are about 120°. The O–P–O angles are distorted tetrahedral (from 102·4 to 115·2°).

Information on the ring geometry is given in Table 4, which lists the equations of the least-squares planes. The angle between (i) and (ii) is 31·1 as compared with 54·8° between (i) and (iii). This illustrates the distortion of the chair from the cyclohexane configuration which is considerably flattened at the phosphorus end.

There are no intermolecular contacts short enough to affect the conformation of the ring. The shortest

Table 4. *Details of ring geometry*

Equations of the least-squares planes are given in the form $lx + my + nz = d$, the axes being defined by $x = xa$, $y = yb$, $z = zc$.

Plane	Atoms in the plane	l	m	n	d
(i)	O(1), O(3), C(4), C(6)	0·8087	−0·5793	0·1023	0·6642
(ii)	P(2), O(1), O(3)	0·7074	−0·5660	−0·4234	−1·1470
(iii)	C(4), C(5), C(6)	0·4804	−0·4575	−0·7483	−3·5888

Table 5. *Comparison of the average* P–O *bond in* PRO_3 *tetrahedra with shortening of the single* P–R *bond*

R is the atom in the axial position; $r(P) + r(R)$ is the sum of Pauling's (1973) single-bonded radii for P and R atoms corrected for electronegativity difference (Schomaker & Stevenson, 1941); $d(P–R)$ is the average (for n averaged structures) P–R bond length; $r(P) + r(R) − d(P–R)$ is the shortening of the single P–R bond by the π-backbonding; $d(P–O)$ is the average P–O bond length (averaged for n structures); and n is the number of structures.

R	$r(P) + r(R)$	$d(P–R)$	$r(P) + r(R) − d(P–R)$	$d(P–O)$	n	References
S	2·10	2·10 (1)	0	1·53 (1)	1	(1)
C	1·83	1·83 (2)	0	1·53 (2)	3	(2), (3), (4)
Br	2·18	2·17 (1)	0·01	1·52 (1)	1	(5)
Cl	2·01	2·00 (1)	0·01	1·48 (1)	1	(6)
N	1·72	1·68 (1)	0·04	1·54 (1)	2	(7), (8)
O	1·63	1·56 (1)	0·07	1·54 (1)	3	(9), (10), (11)

(1) This work; (2) Haque, Caughlan, Hargis & Bentrude (1970); (3) Killean, Lawrence & Magennis (1971); (4) Drew & Rodgers (1972); (5) Beineke (1969); (6) Silver & Rudman (1972); (7) Cameron, Karolak-Wojciechowska & Zwierzak (1976); (8) Cameron, Gałdecki & Karolak-Wojciechowska (1976); (9) Murayama & Kainosho (1969); (10) Geise (1967); (11) Haque, Caughlan & Moats (1970).

intermolecular distance (3·751 Å) is between C(2) and C(2)' in the molecule displaced by $-x, -y, -z+1$.

The packing of the molecules in the crystal is shown in Fig. 3.

Discussion

The molecular configuration of bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinanyl) sulphide is contrary to that predicted by Katritzky, Nesbit, Michalski, Tulimowski & Zwierzak (1970) with the bridging sulphur atom in the equatorial position.

In the title compound the bond distances and angles are not significantly different from those found in the other 1,3,2-dioxaphosphorinane rings; however, the rings are more flattened at the phosphorus ends (31·1°). Such ring deformation decreases the steric repulsion between the axial substituent at the phosphorus atom and the two hydrogen atoms at the 4,6-diaxial positions. Another way to reduce the steric strain mentioned above is by bending the P–R bond on the outside away from the axial hydrogen atoms, thus increasing the angles O(1)–P(2)–R and O(3)–P(2)–R.

If the axial substituent is linked to P(2) by a single bond, considerable flattening of the ring is observed. The angles O(1)–P(2)–R and O(3)–P(2)–R are smaller than tetrahedral (the average value for 14 known rings is 105·5°). The steric repulsion between R and the axial hydrogens on C(4) and C(6) is here reduced by decreasing the dihedral angle between plane (i) containing atoms O(1),O(3),C(4),C(6) and plane (ii) containing atoms O(1),O(3),P(2). This angle decreases in the following order: R = OH (Murayama & Kainosho, 1969); R = OCH₃ (Rodgers, White & Verkade, 1971; Grand, Martin, Robert & Tordjman, 1975); R = N–C(CH₃)₃ (Bartczak, Christensen, Kinas & Stec, 1976a); R = Br (Beineke, 1969); R = OC₆H₅ (Geise, 1967; Grand & Robert, 1975);

R = O–P⟨ (Bukowska-Strzyżewska, Dobrowolska &

Michalski, 1976); R = Cl (Silver & Rudman, 1972); R = NC₆H₅ (Cameron, Gałdecki & Karolak-Wojciechowska, 1976); R = NCO (Cameron, Karolak-Wojciechowska & Zwierzak, 1976); R = CH₃ (Haque, Caughlan, Hargis & Bentrude, 1970); R = S–P⟨

(this work); R = C(C₆H₅)₃ (Drew & Rodgers, 1972); and is 41·8, 38·4(ave.), 37·8, 36·7(ave.), 36·7(ave.), 36·1, 34·6, 34·2, 33·7, 33·5, 31·1 and 3·7° respectively. The increasing size of these R substituents, or decreasing R–P(2) distance, involves greater flattening of the rings.

If the axial substituent R is linked by a double bond to P(2), strong flattening of the ring is not observed. For R = Se and R = S the dihedral angles (i)–(ii) are 43·9 and 45·7° respectively and the angles O(1)–P(2)–R and O(3)–P(2)–R are larger than tetrahedral (Dutasta, Grand & Robert, 1974; Bartczak, Christensen, Kinas & Stec, 1976b).

In Table 5 is a comparison of the average P–O bond in PRO₃ tetrahedra with the shortening of

the single P–R bond in the above-mentioned structures. It shows that the single P–R bond is not considerably shortened by the π-backbonding, if R = S,C,Br,Cl, but is much shorter than the sum of single-bonded radii if R is N or O. From column 5 of Table 5 it is obvious that the average P–O bond length is nearly the same, regardless of the π-bond order in the P–R bond.

In the title compound there are comparatively weak P–S bridging bonds and the P–S–P angle is similar to that found in phosphorus sulphides (Corbridge, 1974).

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