

The Crystal and Molecular Structure of 2,5-Dithio-1-phenyl-1-thiophosphorus(V)-cyclopentane

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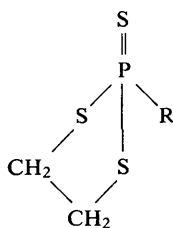
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The crystal and molecular structure of 2,5-dithio-1-phenyl-1-thiophosphorus(V)cyclopentane has been determined from X-ray data by direct methods and confirmed by Patterson techniques. The structure was refined by full-matrix least-squares methods using three-dimensional data. The unit cell is monoclinic, space group $P2_1/m$ with $a=9.301$, $b=7.241$, $c=7.846$ Å, $\beta=99^\circ 27'$ and $Z=2$. Final R factor based on 944 independent observed reflexions is 9.1%. The phosphorus atom is surrounded by three sulphur atoms and an aromatic carbon in a tetrahedral arrangement, which is slightly distorted by the P=S bond and by the inclusion of phosphorus in a 5-membered ring. A plane of symmetry passes through the phenyl and P=S groups and bisects the heterocyclic ring. Phosphorus-to-heterocyclic-sulphur distances 2.087 Å are considered to be normal single bonds although they are much shorter than the Pauling single-bond value even when an electronegativity correction has been applied. The P=S distance of 1.936 Å is longer than the sum of the Pauling double-bond radii when corrected for the difference in electronegativity, but is shorter than the values found in several diphosphine disulphides. The heterocyclic ring is strained with angles S-P-S=98.5, P-S-C=99.4, S-C-C=119.1° and a C-C distance of 1.459 Å. Further evidence shows that the van der Waals radius of sulphur should be 1.72–1.73 Å instead of the 1.85 Å value suggested by Pauling.

Introduction

As part of a series of structural studies on a group of new compounds



prepared by Professor R. Schmutzler and his co-workers, 2,5-dithio-1-phenyl-1-thiophosphorus(V)cyclopentane was analysed to obtain information on the P-S bonds and to explain the nuclear magnetic resonance data.

Experimental

Crystals were provided by Dr S. C. Peake. Recrystallization from diethyl ether gave colourless crystals (68° melting point) in the form of pseudo-hexagonal blocks which revealed straight extinction.

A 0.44 × 0.27 × 0.28 mm crystal was used to obtain oscillation and Weissenberg photographs; equi-inclination Weissenberg data were collected for layers $h0l$ to $h7l$ with a Stoë automatic diffractometer. The crystal was aligned by means of the $0k0$ reflexions. Of the 1111 independent reflexions measured, 944 were greater than 2.3 times their standard deviation of intensity and were treated as observed. No correction was made for absorption or extinction.

Crystal data

$S_3PC_8H_9$, $M=233.23$

Monoclinic,

$a=9.301$, $b=7.241$, $c=7.846$, all ± 0.003 Å;

$\beta=99^\circ 27' \pm 15'$, $U=521.2$ Å³, $F_{000}=240$,

λ (Cu $K\alpha$)=1.5418 Å, μ (Cu $K\alpha$)=72.1 cm⁻¹,

$Z=2$, $D_c=1.480$ g.cm⁻³.

$D_m=1.46$ g.cm⁻³ (by flotation in aqueous potassium iodide).

Absent reflexions: $0k0$ when k odd. Space group $P2_1$ or $P2_1/m$. The latter was indicated by an $N(z)$ statistical test and confirmed by the subsequent refinement.

Structure determination

All calculations were carried out with the Loughborough University X-ray (*LUX*) system of *FORTAN* programs on the University 32K ICL 1905 computer. An adaption of the symbolic-addition programs of Ahmed, Hall, Pippy & Huber (1966) was used. The procedure is described in detail by Lee & Goodacre (1971*b*).

A Wilson (1942) plot gave overall scale and temperature factors. The distribution statistics of the normalized structure amplitudes were compared with the theoretical values (Karle, Hauptman, Karle & Wing, 1958) and confirmed that the structure was centrosymmetric. The program automatically selected and assigned positive signs to reflexions $\bar{1}06$, $\bar{3}05$ and 351 . The signs of the 88 largest $|E|$ values above 1.8 were estimated first using single E triplets, with a minimum probability limit of 98%. In the second stage 97 out of the $|E|$ values (1.8–1.4) were signed

with the minimum acceptable probability set at 97%.

A three-dimensional *E* map computed on the 185 signed reflexions clearly showed the positions of the sulphur atoms, phosphorus atoms and 7 of the 8 carbon atoms. From geometrical considerations the 8th carbon atom was located on a much lower peak, which was approximately the same height as several unexplained background peaks.

As a check a three dimensional Patterson summation was performed and interpreted, giving an orientation of the molecule that was identical with that obtained from the *E* map.

The molecule must possess a mirror plane that passes through the P=S atoms and is perpendicular to the heterocyclic ring. The benzene ring could lie either in the mirror plane or normal to it. The former orientation for the aromatic ring was confirmed by the *E* map and the Patterson synthesis.

Structure refinement

All calculations were performed with adapted NRC data reduction and Fourier programs (Ahmed, Hall, Pippy & Huber, 1966) and the full-matrix least-squares program *LEE-ORFLS* [a version of the Busing, Martin & Levy (1962) program *ORFLS*].

A structure-factor calculation was performed with the S, P and C atoms in the positions suggested by the *E* map. Individual isotropic temperature factors were $B=3.0 \text{ \AA}^2$ for P and S atoms and $B=4.0 \text{ \AA}^2$ for C atoms. Atomic scattering factors were those of Hanson, Herman, Lea & Skillman (1964). The curves for P and S were modified for the real part of anomalous dispersion (Dauben & Templeton, 1955). The agreement factor *R* was 24.9%.

Five cycles of least-squares refinement with anisotropic temperature factors for the P and S atoms, and a Cruickshank (1965) type of weighting scheme:

$$w = \frac{1}{A + B|F_o| + C|F_o|^2}$$

reduced *R* to 12.2%.

A difference Fourier map showed approximate positions for the H atoms, and these were calculated at a distance of 1.075 Å from the carbon atoms to which they are attached, and included in the calcula-

tions in fixed positions with isotropic temperature factors $B=6.0 \text{ \AA}^2$.

The C atoms were refined anisotropically and this reduced *R* to 10.1%. But the C(1)–C(1') bond length, which had previously been close to the value found in the related compound 2,5-dithio-1-chloro-1-thiophos-

Table 1. *Final atomic coordinates and e.s.d.'s*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
S(1)	0.2231 (2)	0.9684 (2)	0.5380 (2)
S(2)	0.0882 (2)	0.7500	0.8608 (3)
P	0.2361 (2)	0.7500	0.7135 (2)
C(1)	0.1498 (11)	0.8508 (17)	0.3485 (13)
C(2)	0.4198 (6)	0.7500	0.8299 (8)
C(3)	0.5391 (8)	0.7500	0.7425 (10)
C(4)	0.6778 (8)	0.7500	0.8353 (14)
C(5)	0.7011 (9)	0.7500	1.0147 (13)
C(6)	0.5835 (10)	0.7500	1.1027 (11)
C(7)	0.4415 (8)	0.7500	1.0072 (9)

Table 2. *Calculated positions of hydrogen atoms*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
H(1)	0.0382	0.8942	0.3147
H(11)	0.2101	0.8942	0.2498
H(3)	0.5225	0.7500	0.6036
H(4)	0.7697	0.7500	0.7681
H(5)	0.8103	0.7500	1.0854
H(6)	0.6004	0.7500	1.2416
H(7)	0.3492	0.7500	1.0737

Hydrogen atoms were assigned an isotropic temperature factor of $B=6.0 \text{ \AA}^2$.

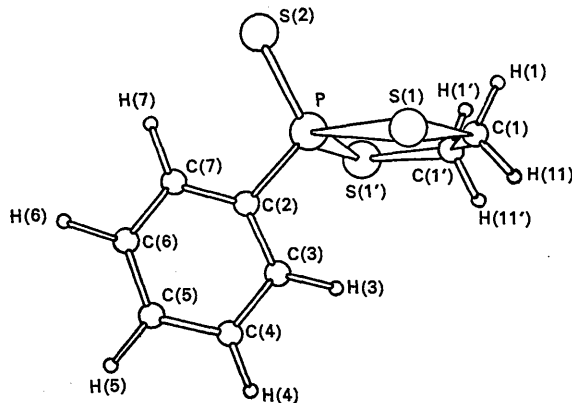


Fig. 1. View of the molecule.

Table 3. *Final temperature-factor parameters and e.s.d.'s*

$$TF = \exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.0170 (2)	0.0158 (3)	0.0193 (3)	-0.0029 (2)	-0.0001 (2)	0.0070 (2)
S(2)	0.0088 (2)	0.0293 (6)	0.0201 (3)	0.0000	0.0076 (2)	0.0000
P	0.0073 (2)	0.0074 (3)	0.0128 (2)	0.0000	0.0039 (2)	0.0000
C(1)	0.0439 (2)	0.0332 (2)	0.0183 (1)	0.0201 (2)	-0.0026 (1)	-0.0041 (1)
C(2)	0.0075 (6)	0.0053 (10)	0.0150 (10)	0.0000	0.0036 (6)	0.0000
C(3)	0.0090 (8)	0.0174 (16)	0.0199 (13)	0.0000	0.0044 (8)	0.0000
C(4)	0.0080 (7)	0.0148 (16)	0.0331 (20)	0.0000	0.0062 (10)	0.0000
C(5)	0.0098 (9)	0.0113 (15)	0.0338 (22)	0.0000	-0.0023 (11)	0.0000
C(6)	0.0151 (12)	0.0147 (16)	0.0205 (15)	0.0000	-0.0031 (10)	0.0000
C(7)	0.0103 (8)	0.0111 (13)	0.0166 (11)	0.0000	0.0034 (7)	0.0000

phorus(V)cyclopentane (Lee & Goodacre, 1971b) suddenly changed with the introduction of anisotropic temperature factors. This bond length depends only on the y/b coordinate of C(1) and the high correlation between this coordinate and the anisotropic temperature factor arises because the data were collected up [010]. As a result, an isotropic temperature factor was

Table 4 (cont.)

Table with 12 columns of numerical data representing structure factors for various hkl reflections, including values for h, k, l, Fo, and Fc.

Table 4. Observed and calculated structure factors

Table with 12 columns of numerical data representing observed and calculated structure factors for various hkl reflections, including values for h, k, l, Fo, and Fc.

used for C(1). Further refinement restored the C(1)-C(1') bond length to its former value.

Final weight constants of A = 1.000, B = -0.054 and C = 0.047, were used and C(1) was refined anisotropically but its positional parameters were not varied. New

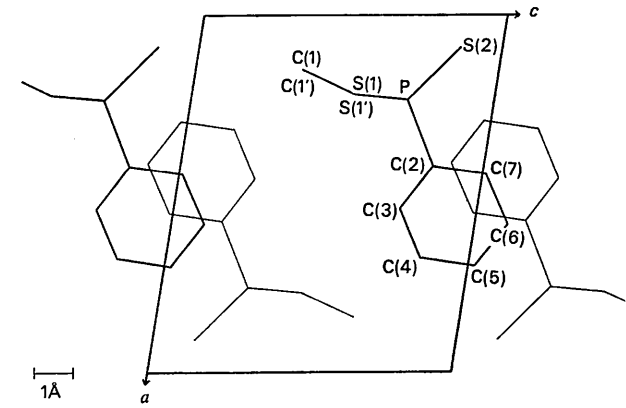


Fig. 2. Contents of one unit cell as seen down [010].

Table 5. Agreement analysis

Table with 6 columns: F_obs, Number of planes, R, sin theta/lambda, Number of planes, and R. It lists data for various reflection ranges from 0-3 to >30.

hydrogen positions were calculated, and the reliability index converged at $R=9.1\%$.

The predicted signs of the 185 strong reflexions were all found to be correct. Results are presented in Tables 1 to 8.

Table 6. Bond lengths and *e.s.d.*'s

P—S(1)	2.087 (2) Å
P—S(2)	1.936 (2)
P—C(2)	1.801 (6)
S(1)—C(1)	1.751 (11)
C(1)—C(1')	1.459 (25)
C(2)—C(3)	1.397 (9)
C(3)—C(4)	1.373 (11)
C(4)—C(5)	1.389 (15)
C(5)—C(6)	1.386 (13)
C(6)—C(7)	1.407 (11)
C(7)—C(2)	1.373 (9)

Table 7. Bond angles and *e.s.d.*'s

S(2)—P—S(1)	115.1 (1)°
S(2)—P—C(2)	113.9 (2)
S(1)—P—S(1')	98.5 (1)
S(1)—P—C(2)	106.4 (2)
P—S(1)—C(1)	99.4 (4)
S(1)—C(1)—C(1')	119.1 (8)
P—C(2)—C(3)	121.0 (4)
P—C(2)—C(7)	118.9 (4)
C(3)—C(2)—C(7)	120.1 (5)
C(2)—C(3)—C(4)	119.5 (6)
C(3)—C(4)—C(5)	120.9 (7)
C(4)—C(5)—C(6)	120.1 (7)
C(5)—C(6)—C(7)	118.9 (6)
C(6)—C(7)—C(2)	120.6 (5)

Table 8. Short intermolecular approaches

(a) Involving a sulphur atom.

Generated atom	Symmetry operation	Distance
S(1)···H(1)	(i)	3.03 Å
S(1)···H(6)	(ii)	2.99
S(2)···C(1)	(i)	3.84
S(2)···C(1)	(iii)	3.84
S(2)···H(4)	(iv)	2.93
H(1)··S(1)	(i)	3.03
H(6)··S(1)	(ii)	2.99
C(1)··S(2)	(i)	3.84
H(4)··S(2)	(v)	2.93

(b) Other short intermolecular approaches.

C(1)··H(7)	(vi)	3.15
C(1)··H(4)	(ii)	3.16
H(7)··C(1)	(vii)	3.15
H(7)··C(1)	(viii)	3.15
H(4)··C(1)	(ii)	3.16
H(4)··C(1)	(ix)	3.16

Key to symmetry operations:

(i)	$-x, 2-y, 1-z$
(ii)	$1-x, 2-y, 1-z$
(iii)	$-x, y-\frac{1}{2}, 1-z$
(iv)	$x-1, y, z$
(v)	$1+x, y, z$
(vi)	$x, y, z-1$
(vii)	$x, y, 1+z$
(viii)	$x, 1\frac{1}{2}-y, 1+z$
(ix)	$1-x, y-\frac{1}{2}, 1+z$

Discussion

A view of the molecule is given in Fig. 1. The contents of one unit cell as seen down [010] are shown in Fig. 2. Bond lengths and angles with their estimated standard deviations are listed in Tables 6 and 7. The standard deviations of the C(1)—C(1') bond, and of angles involving S(1') and C(1'), were calculated differently from the others, to allow for the mirror plane of symmetry passing through the heterocyclic ring (Cruickshank & Robertson, 1953).

The environment of the phosphorus atom is roughly tetrahedral. Bond length P=S(2) of 1.936 ± 0.002 Å is shortened by backbonding from a full sulphur *p* orbital to an empty phosphorus *d* orbital. The sum of Pauling's (1960) double-bonded radii for P and S is 1.94 Å. If the Schomaker–Stevenson (1941) correction for electronegativity difference is applied, the distance becomes 1.916 Å. A considerably shorter P=S bond of 1.910 Å occurs in the analogous 2,5-dithio-1-chloro-1-thiophosphorus(V)cyclopentane (Lee & Goodacre, 1971*b*). In this compound the high electronegativity of chlorine probably localizes the *d* orbitals on the phosphorus atom and causes more effective π overlap and hence a shorter bond. The observed P=S(2) value compares with values of 1.95 Å in bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969), 1.95 Å bis(cyclopentamethylene)diphosphine disulphide (Lee & Goodacre, 1970), 1.95 and 1.97 Å in tetramethyldiphosphine disulphide (Lee & Goodacre, 1971*a*), and 1.94 Å in tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961). The P=S bond length reported for 1,2-dimethyl-1,2-diphenyldiphosphine disulphide (Wheatley, 1960) of 1.98 Å is much longer.

The P—S(1) distance of 2.087 ± 0.002 Å is much longer than the P—S values of 2.051 Å in 2,5-dithio-1-chloro-1-thiophosphorus(V)cyclopentane. Values in both these compounds are very much shorter than the sum of Pauling's single-bonded radii (2.14 Å) and the electronegativity corrected value of 2.116 Å.

The S(1)—C(1) bond length is 1.75 Å, which is short compared with the sum of Pauling's single-bonded radii (1.81 Å), values of 1.81 and 1.83 Å in 2,5-dithio-1-chloro-1-thiophosphorus(V)cyclopentane and 1.818 Å in methanethiol CH₃SH (Kilb, 1955). Strain in the heterocyclic ring probably accounts for this shortening. The C(1)—C(1') bond of 1.46 Å is appreciably shorter than the normal single-bond distance, but is fairly close to the value of 1.47₅ Å in the chlorine analogue.

The P—C(2) distance of 1.801 ± 0.006 Å is close to the values of 1.80, 1.82 and 1.82 Å in tetramethyldiphosphine disulphide, 1.81 Å in bis(cyclopentamethylene)diphosphine disulphide, 1.82 Å in bis(cyclo-tetramethylene)diphosphine disulphide, 1.82 Å in 1,2-dimethyl-1,2-diphenyldiphosphine disulphide, 1.82 and 1.84 Å in tetra-ethyldiphosphine disulphide. The sum of Pauling's (1960) single-bond radii for P and C is 1.872 Å which, when corrected for the difference in

electronegativity, gives a bond length of 1.84 Å. C–C distances in the aromatic ring range from 1.37 to 1.41 Å.

The tetrahedral arrangement of bonds round the phosphorus is distorted by the shortness of the P=S(2) bond. This produces three angles, S(2)–P–S(1), S(2)–P–S(1') and S(2)–P–C(2), greater than tetrahedral (115.1, 115.1 and 113.9° respectively). The remaining three angles are less than tetrahedral. Angle S(1)–P–S(1') is further reduced by the inclusion of the phosphorus atom in a 5-membered heterocyclic ring.

The heterocyclic ring is strained. This puckers the ring and distorts the angles P–S(1)–C(1) to 99.4°, and S(1)–C(1)–C(1') to 119.1°. The equation to the least-squares plane through the heterocyclic ring (calculated by the method of Schomaker, Waser, Marsh & Bergman, 1959) is $9.20X + 0.00Y - 2.42Z = 0.60$, where X , Y and Z refer to the unit-cell axes a , b and c . Distances of the atoms from the plane are P=0.157 Å, S(1) and S(1')=–0.147 Å, and C(1) and C(1')=0.069 Å.

All interatomic distances up to 4.0 Å were calculated. Non-bonded distances less than the sum of the van der Waals radii which occur within one molecule were examined. The van der Waals radii used are those of Pauling (1960): S=1.85, P=1.9, CH₂=2.0 Å, half thickness of aromatic ring=1.70 Å, H=1.2 Å. These close approaches are all unavoidable. Three involve S and H atoms: S(1)···H(1)=2.31, S(1)···H(11)=2.31, S(2)···H(7)=2.71 Å. Despite the shortness of these distances the possibility of intramolecular hydrogen bonding is precluded by angles C(1)–H(1)···S(1)=46.5, C(1)–H(11)···S(1)=46.5 and C(7)–H(7)···S(2)=114.0°.

Short intermolecular contacts involving a sulphur atom are listed in Table 8(a). It has been suggested that the Pauling value (1.85 Å) for the van der Waals radius of sulphur is too long, and a value of 1.72–1.73 Å is more appropriate (Fava Gasparri, Nardelli & Villa, 1967; Nardelli, Fava Gasparri, Giraldi Battistina & Domiano, 1966; Ždanov & Zvonkova, 1950; van der Helm, Lessor & Merritt, 1960; Lee & Bryant, 1969a & b; Lee & Goodacre, 1970). With this smaller value, these contacts all become normal. Other short intermolecular approaches are given in Table 8(b) but no significance is attached to them.

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