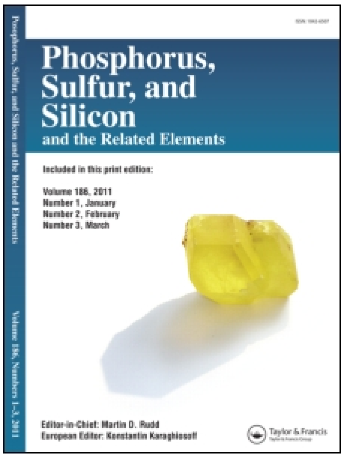


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOSULFUR COMPOUNDS. XLVI[1] CRYSTAL AND MOLECULAR STRUCTURE OF 2-DIPHENYL-THIOPHOSPHINOYL-1,3,5-TRITHIANE

Marian Mikołajczyk[a]; Piotr Bałczewski[a]; Michał W. Wieczorek[b]; Grzegorz Bujacz[b]; Michail Y. Antipin[c]; Yurij I. Struchkov[c]
[a] Department of Organic Sulfur Compounds, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lódź, Boczna 5, Poland [b] Institute of General Chemistry, Technical University, Lódź, żwirki 36, Poland [c] Institute of Organoelement Compounds, Academy of Sciences USSR, Moscow, USSR

To cite this Article Mikołajczyk, Marian , Bałczewski, Piotr , Wieczorek, Michał W. , Bujacz, Grzegorz , Antipin, Michail Y. and Struchkov, Yurij I.(1988) 'ORGANOSULFUR COMPOUNDS. XLVI[1] CRYSTAL AND MOLECULAR STRUCTURE OF 2-DIPHENYL-THIOPHOSPHINOYL-1,3,5-TRITHIANE', Phosphorus, Sulfur, and Silicon and the Related Elements, 37: 3, 183 — 188

To link to this Article: DOI: 10.1080/03086648808079035

URL: http://dx.doi.org/10.1080/03086648808079035

Phosphorus and Sulfur, 1988, Vol. 37, pp. 183–188
Reprints available directly from the publisher
Photocopying permitted by license only

ORGANOSULFUR COMPOUNDS. XLVI[1] CRYSTAL AND MOLECULAR STRUCTURE OF 2-DIPHENYL-THIOPHOSPHINOYL-1,3,5-TRITHIANE

MARIAN MIKOŁAJCZYK† and PIOTR BAŁCZEWSKI
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-362 Łódź, Boczna 5, Poland

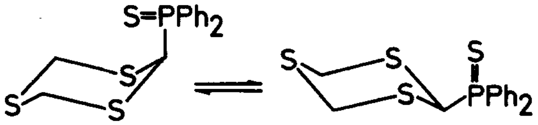
MICHAŁ W. WIECZOREK and GRZEGORZ BUJACZ
Institute of General Chemistry, Technical University, 90-924 Łódź, Żwirki 36, Poland

MICHAIL Y. ANTIPIN and YURIJ I. STRUCHKOV
Institute of Organoelement Compounds, Academy of Sciences USSR, Moscow 117312, Vavilov Street 28, USSR

(Received December 8, 1987)

The crystal structure of the title compound has been determined by direct methods and refined by least-squares to $R = 0.0462$; monoclinic space group $P2_1/c$, $a = 15.0597(9)$, $b = 10.758(7)$, $c = 10.5561(11)$Å, $\beta = 93.809(7)°$. The trithiane adopts a chair conformation with the diphenylthiophosphinoyl group being equatorial.

Recently, we have been interested in the conformation of heteroanes containing the organophosphorus substituents at the anomeric carbon atom.[2–5] In contrast to the 2-phosphoryl substituted 1,3-di- and 1,3,5-trithianes, which adopt axial conformation both in solution and in the crystal,[5,6] the thiophosphoryl and selenophosphoryl derivatives exist in solution as a mixture of axial and equatorial conformers as evidenced by ^{1}H-, ^{13}C and ^{31}P-NMR studies.[4] Thus, for example, the ^{31}P-NMR signal of the title compound-2-diphenylthiophosphinoyl-1,3,5-trithiane (**1**)-is split at −100°C into two lines of similar intensity which correspond most probably to its axial and equatorial conformers.



1-ax **1**-eq

In this paper we would like to report the results of X-ray analysis of this trithiane which revealed that it exists in the crystal in a chair conformation with the Ph$_2$P(S)-group being equatorial.

---

† Author to whom all correspondence should be addressed.

RESULTS AND DISCUSSION

A three dimensional view of the molecule investigated and the atom numbering are shown in Figure 1. The final positional parameters and the equivalent isotropic parameters for non-hydrogen atoms are given in Table I. Hydrogen atom positional parameters with isotropic temperature factors are listed in Table II. Tables III and IV contain bond distances and angles.†

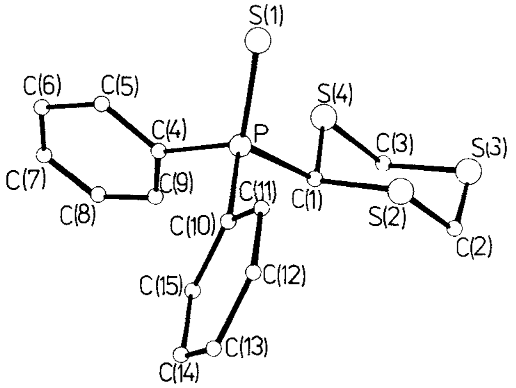


FIGURE 1 The solid state conformation of 2-diphenylthiophosphinoyl-1,3,5-trithiane (**1**).

TABLE I

Positional parameters ($\times 10^4$) for the nonhydrogen atoms and their isotropic temperature factors ($Å^2 \times 10^3$)

	X	Y	Z	U
P	7571(1)	8873(1)	2161(1)	41(1)
S(2)	5716(1)	8947(2)	1803(2)	63(1)
S(3)	4595(1)	6605(2)	1173(2)	85(1)
S(4)	6463(1)	6651(2)	2498(2)	66(1)
S(1)	7294(1)	9539(2)	3803(1)	61(1)
C(1)	8663(3)	7934(4)	1430(5)	43(2)
C(2)	4983(4)	7851(6)	241(7)	77(3)
C(3)	5631(4)	5805(6)	1503(7)	78(3)
C(4)	8559(3)	7901(5)	2249(5)	45(2)
C(5)	9221(4)	8178(5)	3163(6)	59(2)
C(6)	9966(4)	7478(7)	3275(7)	81(3)
C(7)	10088(4)	6490(7)	2473(7)	76(3)
C(8)	9433(4)	6196(6)	1591(7)	75(3)
C(9)	8665(4)	6899(6)	1450(6)	64(2)
C(10)	7749(3)	10000(5)	1001(5)	44(2)
C(11)	7406(3)	11258(5)	1191(6)	53(2)
C(12)	7528(4)	12183(8)	1333(7)	73(3)
C(13)	8010(5)	11964(7)	−723(7)	84(3)
C(14)	8350(6)	10803(7)	−910(7)	99(4)
C(15)	8214(5)	9845(6)	−47(6)	73(3)

An inspection of Figure 1 reveals that the six-membered trithiane ring in **1** has a chair conformation with the diphenylthiophosphinoyl substituent at the anome-

---

† The structure factors and anisotropic thermal parameters (Table V) are deposited with the British Library Lending Division as Supplementary Material.

TABLE II

Hydrogen atom positional parameters ($\times 10^4$) with isotropic temperature factors (Å $\times 10^3$)

	X	Y	Z	U
H(1)	6601	7573	635	51
H(2)	5304	7493	−425	96
H(2)	4476	8296	−123	96
H(3)	5881	5659	703	91
H(3)	5519	5023	1902	91
H(5)	9145	8849	3746	73
H(6)	10444	7688	3915	88
H(7)	10617	5992	2568	82
H(8)	9527	5533	1006	85
H(9)	9200	6647	837	79
H(11)	7079	11418	1024	65
H(12)	7294	12989	477	86
H(13)	6122	12631	−1294	96
H(14)	8647	10643	−1670	125
H(15)	8462	9038	−181	79

TABLE III

Bond lengths (Å)

P-S(1)	1.947(2)	P–C(1)	1.829(5)
P-C(4)	1.816(5)	P–C(10)	1.817(5)
S(2)–C(1)	1.814(5)	S(2)–C(2)	1.808(7)
S(3)–C(2)	1.784(7)	S(3)–C(3)	1.795(7)
S(4)–C(1)	1.814(5)	S(4)–C(3)	1.819(7)
C(4)–C(5)	1.374(7)	C(4)–C(9)	1.384(8)
C(5)–C(6)	1.374(9)	C(6)–C(7)	1.374(10)
C(7)–C(8)	1.348(9)	C(8)–C(9)	1.382(9)
C(10)–C(11)	1.388(7)	C(10)–C(15)	1.370(8)
C(11)–C(12)	1.370(9)	C(12)–C(13)	1.379(10)
C(13)–C(14)	1.369(11)	C(14)–C(15)	1.399(10)

TABLE IV

Bond angles (°)

C(1)–P–S(1)	112.3(2)	S(1)–P–C(4)	113.6(2)
C(1)–P–C(4)	106.9(2)	S(1)-P–C(10)	112.8(2)
C(1)–P–C(10)	104.5(2)	C84)–P–C(10)	106.8(2)
C(1)–S(2)–C(2)	98.8(3)	C(2)–S(3)–C(3)	99.0(3)
C(1)–S(4)–C(3)	99.5(3)	P–C(1)–S(2)	108.0(3)
P–C(1)–S(4)	108.1(3)	S(2)–C(1)–S(4)	114.9(3)
S(2)–C(2)–S(3)	115.5(4)	S(3)–C(3)–S(4)	115.3(3)
P–C(4)–C(5)	117.7(4)	P–C(4)–C(9)	123.0(4)
C(5)–C(4)–C(9)	119.2(5)	C(4)–C(5)–C(6)	120.4(6)
C(5)–C(6)–C(7)	119.9(6)	C(6)–C(7)–C(8)	120.0(6)
C(7)–C(8)–C(9)	121.0(6)	C(4)–C(9)–C(8)	119.3(5)
P–C(10)–C(11)	118.8(4)	P–C(10)–C(15)	121.2(4)
C(11)–C(10)–C(15)	120.0(5)	C(10)–C(11)–C(12)	119.6(6)
C(11)–C(12)-C(13)	121.1(6)	C(12)–C(13)–C(14)	119.2(7)
C(13)–C(14)–C(15)	120.4(7)	C(10)–C(15)–C(14)	119.6(6)

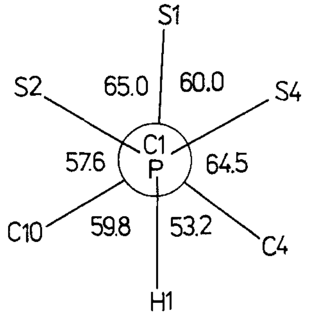


FIGURE 2 Newman projection around C(1)—P bond showing the relevant torsion angles (°) in **1**.

ric carbon atom C(1) in equatorial position. Moreover, the Newman projection around the C(1)—P bond (see Figure 2) clearly indicates that the thiophosphoryl sulfur atom S(1) is almost symmetrically situated between the both ring sulfur atoms S(2) and S(4). The corresponding distances are 3.659 and 3.594 Å, respectively.

The deformations of the trithiane ring in **1** in relation to the plane of symmetry are shown below:

$$\Delta C_S(S4) = 0.7°; \quad \Delta C_S(C1) = 1.6°; \quad \Delta C_S(C2) = 2.3°$$

The two-fold asymmetry parameters are calculated similarly and are as follows:

$$\Delta C_2(C1—S2) = 2.7°; \quad \Delta C_2(C1—S4) = 0.9°; \quad \Delta C_2(S2—C2) = 2.1°$$

In order to estimate the deviations of the trithiane ring in **1** from an ideal chair conformation it was necessary to calculate the most advantageous plane passing

TABLE V

Anisotropic temperature factors ($Å^2 \times 10^3$) for the nonhydrogen atoms

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	45(1)	39(1)	40(1)	0(1)	1(1)	3(1)
S(2)	42(1)	54(1)	92(1)	2(1)	−2(1)	2(1)
S(3)	60(1)	93(1)	104(1)	−7(1)	24(1)	−31(1)
S(4)	79(1)	54(1)	67(1)	14(1)	12(1)	−7(1)
S(1)	80(1)	59(1)	43(1)	−9(1)	4(1)	14(1)
C(1)	41(3)	40(3)	48(3)	−0(2)	9(2)	2(2)
C(2)	47(3)	90(5)	92(5)	4(4)	−9(3)	−15(4)
C(3)	88(5)	56(4)	94(5)	−2(4)	31(4)	−28(4)
C(4)	45(3)	46(3)	43(3)	6(2)	1(2)	2(3)
C(5)	46(3)	59(4)	69(4)	−4(3)	−11(3)	−2(3)
C(6)	56(4)	91(5)	92(5)	6(4)	−27(4)	3(4)
C(7)	43(3)	89(5)	96(5)	20(4)	−2(4)	19(4)
C(8)	68(4)	74(5)	83(5)	−11(4)	9(4)	33(4)
C(9)	58(4)	67(4)	63(4)	−10(3)	−7(3)	22(3)
C(10)	42(3)	44(4)	44(3)	4(2)	−8(2)	−8(3)
C(11)	41(3)	43(3)	76(4)	13(3)	−4(3)	−1(3)
C(12)	58(4)	56(4)	105(5)	27(4)	−16(4)	−4(3)
C(13)	86(5)	81(5)	83(5)	41(4)	−8(4)	−16(4)
C(14)	155(8)	88(6)	57(4)	19(4)	31(5)	−1(6)
C(15)	105(5)	60(4)	57(4)	3(3)	19(4)	5(4)

TABLE VI

Geometry of the 1,3,5-trithiane ring in **1**

a. Torsion angles

S4C1S2C2	−64.9(4)	C2S3C3S4	65.8(4)
C1S2C2S3	67.1(4)	S3C3S4C1	−64.9(4)
S2C2S3C3	−67.4(4)	C3S4C1S2	64.3(3)

b. Planes

(i) Plane containing atoms denoted with asterisk

$10.72X - 1.33Y - 7.78Z = 4.11$

S2*	−0.0066	C1	0.8737
C2*	0.0075	S3	−0.9682
C3*	−0.0074		
S4*	0.0066		

(ii) Plane containing atoms: C1S2S4

$3.59X + 6.13Y + 8.12Z = 8.42$

(iii) Plane containing atoms: C2C3S3

$1.81X + 5.90Y + 8.93Z = 5.74$

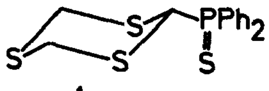
(iv) Plane containing atoms denoted with asterisk

C1*	0.0093	S2	0.9766
C2*	−0.0094	C3	−0.8702
S3*	0.0085		
S4*	−0.0083		

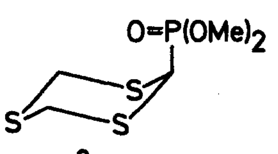
(vi) Plane containing atoms denoted with asterisk

C1*	0.0017	C2	−0.8751
C3*	−0.0017	S4	0.9625
S3*	0.0016		
S2*	−0.0016		

through four atoms in the ring and then to determine the atom deflections from that plane. The results of these calculations are collected in Table VI. It results from these data and the asymmetry parameters that the chair with the atoms C(1), S(2), S(3) and C(3) in one plane (vi) is the one closest to an ideal chair conformation. However, on account of the conformational problems discussed in this paper it is better to take into consideration the slightly deformed chair conformation having a plane passing through the S(2), C(2), S(3) and S(4) atoms (plane i). The angles between this plane and the plane containing C(1), S(2) and S(4) atoms (ii) and the plane formed by C(2), C(3) and S(3) atoms (iii) of 63.6(5)° and 56.3(5)°, respectively, characterize further this chair conformation.



1



2

A comparison of these angles with those found for 2-dimethoxyphosphoryl-1,3,5-trithiane (**2**)[2] with the axial $(MeO)_2P(O)$-group (56.9(5) and 56.7(5)°) points to a *slighter flattening* of the chair conformation at the anomeric carbon atom

C(1) in **1**. The sulfur atom S(3) was found to be deflected from the ring plane (i) in **1** by 0.967(4) Å which corresponds to the almost identical deflection in **2** equal to 0.974(3) Å. The interplane angles (ii/iii) in **1** and **2** are also practically identical amounting to 56.3(5)° and 56.7(5)°, respectively. The angle between the plane (i) and the equatorial C(1)—P bond is 8.8(4)°.

The angles between the phenyl rings and the plane (i) are:

$$C(4), C(5), C(6), C(7), C(8), C(9)/i = 45.0°$$

$$C(10), C(11), C(12), C(13), C(14), C(15)/i = 79.1°$$

The angle between both aromatic rings is equal to 78.6°.

The observed bond lengths for the anomeric carbon atom and S(2) and S(4) of 1.815(5) Å are normal and comparable to those found for **2**. The equatorial C(1)—P bond in **1** is longer by 0.017 Å than the axial C(1)—P bond in **2**.

EXPERIMENTAL

X-Ray Structure Determination of 2-diphenylthiophosphinoyl-1,3,5-trithiane (**1**).
Crystal data. $C_{15}H_{15}PS_4$. $M = 354.48$. *Monoclinic space group* $P2_1/c$, $a = 15.0597(9)$, $b = 10.7581(7)$, $c = 10.5561(11)$ Å; $\beta = 93.809(7)°$, $V = 1706.5$ Å^3, $Z = 4$, $D_m = 1.380$ g cm^{-3}, $D_{cal} = 1.379$ g cm^{-3}, $\mu(\text{MoK}_\alpha) = 0.6182$ mm^{-1}, $\lambda = 0.71069$ Å.

Crystallographic measurements and structure analysis. Single crystals of **1**, mp. 176.5–178.5°C, were grown from chloroform/methanol solution. The space group and appropriate cell parameters were determined from Weissenberg photographs using CuK_α radiation. A small single crystal was mounted on a Syntex $P2_1$ diffractometer and the cell dimensions were refined by MoK_α radiation. The integrated data for structure were collected at −120°C with monochromatic MoK_α radiation at a scan rate of 2°/min and checked by means of the three standard reflections for alignment and crystal stability. Intensity data were collected in the 0–20 mode ($20_{max} = 60°$). No absorption correction was applied [$\mu(\text{MoK}_\alpha) = 0.6182$ mm^{-1}]. After application of the acceptance criterion $J \geqslant 1.96\sigma(J)_Z$, of 2847 collected reflections 1819 were retained for the refinement. The structure was solved by direct methods (MULTAN) and refined by blocked-full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms (SHELX 76). The remaining H atoms were refined with isotropic temperature factors. Convergence was reached at $R = 0.0462$.

ACKNOWLEDGEMENTS

This work was financially supported by the projects CPBP-01.13 and RP-02.10.

REFERENCES

1. Part XLV, see: M. Mikołajczyk, W. Midura and M. Kajtar, *Phosphorus and Sulfur,* in press.
2. M. Mikołajczyk, P. Bałczewski, P. Graczyk, J. Karolak-Wojciechowska, A. Miller, M. W. Wieczorek, M. Y. Antipin and Y. T. Struchkov, *Tetrahedron,* **23,** 4885 (1984).
3. M. Engelhardt, G. Hägele, M. Mikołajczyk, P. Bałczewski and D. Wendisch, *Magn. Resonance in Chem.*, **23,** 18 (1985).
4. M. Mikołajczyk, P. Graczyk and P. Bałczewski, *Tetrahedron Lett.*, **28,** 573 (1987).
5. M. Mikołajczyk, *Pure and Appl. Chem.*, **59,** 983 (1987).
6. E. Juaristi, L. Valle, C. Mora-Uzeta, B. A. Valenzuela, P. Joseph-Nathan and M. F. Frederick, *J. Org. Chem.*, **47,** 5083 (1982); E. Juaristi, L. Valle, B. A. Valenzuela and M. A. Aguilar, *J. Am. Chem. Soc.*, **108,** 2000 (1986).