

Solid state conformation of the anomeric effect in 2-phosphoryl-, 2-thiophosphoryl- and 2-selenophosphoryl-substituted 1,3-dithiolanes ¹

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Abstract

The crystal structure of the title compounds **1–3** have been determined by X-ray diffraction studies. The 1,3-dithiolane ring in all three compounds adopts a twist conformation with the Ph₂P=X group being pseudoaxial. The structural data suggest that the n_S → σ_{C–P}^{*} negative hyperconjugation is responsible for the anomeric effect in 1,3-dithiolanes. © 1997 Published by Elsevier Science S.A.

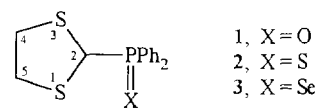
Keywords: Phosphanes; Anomeric effect; Phosphoryldithiolanes; Crystal structure

1. Introduction

Recently, our interest has been devoted to the origin and consequences of the anomeric effect in 1,3-diheteroanones containing second-row atoms bonded to the anomeric carbon atom (for review articles see Ref. [1]). Special attention was paid to 2-phosphoryl-substituted 1,3-dithianes and their thio- and selenophosphoryl analogues [2]. The conformational behaviour and the magnitude of the anomeric effect operating in these systems have been found to be a result of several interactions which stabilize or destabilize the axial position of the organophosphorus substituents at C(2). Among these effects discussed in detail in our recent papers [2,3], the n_O → σ_{C–P}^{*} negative hyperconjugation seems to be an important factor which is responsible for the axial preference of the phosphoryl group.

It is known that the negative hyperconjugation is stronger in furanoses than in pyranoses [4]. Hence, the comparison of five- and six-membered derivatives should also serve as a test for the negative hyperconjugation. Having this in mind, we decided to investigate

the solid state conformation and geometry of the 1,3-dithiolanes **1–3** containing the 2-diphenylphosphinoyl, 2-diphenylthiophosphinoyl and 2-diphenylselenophosphinoyl group. It was expected that anomeric hyperconjugative interactions in the 1,3-dithiolanes **1–3** would be reflected in a shortening of the donor-carbon C(2) bond and in a lengthening of the C(2)–P bond; as well as that, these structural changes will be better visible in the 1,3-dithiolanes than in the corresponding six-membered analogues. The results obtained are reported herein.



2. Experimental

The NMR spectra were recorded on a Bruker AC 200 spectrometer (¹H frequency 200.13 MHz). An Aspect 3000 computer and DISR90 software were used for data processing. Tetramethylsilane (TMS) was used as

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¹ Dedicated to the memory of Professor Yuri Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

an external standard for ^1H NMR, chloroform-*d* signal was used as a reference ($\delta = 77.0$) for ^{13}C NMR, and 85% phosphoric acid was used as an external standard for ^{31}P NMR ($\delta = 0.0$).

2.1. 2-Diphenylphosphinoyl-1,3-dithiolane 1

To a solution of 1,3-dithiolane (1.75 g, 0.0165 mol) in benzene (10 ml) *N*-chlorosuccinimide (2.2 g, 0.0165 mol) was added portionwise under nitrogen. After 1 h stirring, the succinimide formed was filtered off and to a benzene solution and isopropyl diphenylphosphinite (4.125 g, 0.0169 mol) was added. Then, water (10 ml) was added and the layers separated. The organic layer was washed with water (3×5 ml), dried over MgSO_4 and evaporated. The crude dithiolane **1** was crystallized from ethyl acetate to give 2.88 g (57%) of the pure product, m.p. 223 °C.

Anal. Found: C, 58.93; H, 4.73; P, 10.90; S, 19.84. $\text{C}_{15}\text{H}_{15}\text{POS}_2$ Calc.: (306.39): C, 58.80; H, 4.935; P, 10.11; S, 20.93%.

^1H NMR: $(\text{CH}_2)_2$, s, $\delta = 3.14$; CH, d, $\delta = 5.0$, $^2J_{\text{H}-^{31}\text{P}} = 7.23$ Hz, $\text{CH}_{\text{aromatic}}$, m, $\delta = 7.30$ – 7.54 , 7.70 – 7.96 . ^{13}C NMR: $(\text{CH}_2)_2$, $\delta = 39.13$; CH, $\delta = 47.44$, $^1J_{\text{C}-^{31}\text{P}} = 73$ Hz, $\text{CH}_{\text{aromatic}}$, $\delta = 128.18$, 128.39 , 130.22 , 131.61 , 131.78 , 131.94 . ^{31}P NMR: $\delta = 29.98$.

2.2. 2-Diphenylthiophosphinoyl-1,3-dithiolane 2

To a solution of the phosphine oxide **1** (2.5 g, 0.008 mol) in benzene (80 ml) containing phosphorus pentasulphide (3.7 g, 0.017 mol) a solution of diethylamine (1.5 ml) in benzene (12.5 ml) was added within 20 min. The reaction mixture was refluxed for 6 h. After cooling to room temperature, a water solution of potassium carbonate (60 ml, 10%) was added to the reaction

Table 1
Crystal data and experimental details

	Compound 1	Compound 2	Compound 3
Molecular formula	$\text{C}_{15}\text{H}_{15}\text{OS}_2\text{P}$	$\text{C}_{15}\text{H}_{15}\text{S}_3\text{P}$	$\text{C}_{15}\text{H}_{15}\text{SeS}_2\text{P}$
Crystallographic system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
<i>a</i> (Å)	8.287(2)	14.658(2)	9.8390(9)
<i>b</i> (Å)	17.262(2)	9.803(1)	9.3471(5)
<i>c</i> (Å)	22.063(6)	11.1919(8)	17.3899(8)
β (deg)	100.21(2)	98.51(1)	(90)
<i>V</i> (Å ³)	3102(11)	1591(2)	1599.3(2)
<i>Z</i>	8	4	4
<i>D_c</i> (g cm ⁻³)	1.310(2)	1.347(2)	1.534(2)
μ (cm ⁻¹)	4.2	50.4	64.9
Crystal dimensions (mm ³)	0.2 × 0.4 × 0.5	0.4 × 0.4 × 0.6	0.15 × 0.2 × 0.3
Radiation, λ (Å)	Mo K α , 0.71073	Cu K α , 1.54178	Cu K α , 1.54178
Scan mode	ω -2 θ	ω -2 θ	ω -2 θ
Scan width (deg)	0.80 + 0.35 tan θ	1.15 + 0.14 tan θ	0.73 + 0.14 tan θ
Total exposure time (h)	93.5	43.5	46.7
Decline of intensity (%)	0.8	1.8	0.4
Absorption correction			
min.	-	0.8945	0.9185
max.	-	0.9902	0.9995
av.	-	0.9503	0.9679
Transmission (%)			
min.	-	80.02	84.36
max.	-	98.04	99.89
av.	-	90.30	93.68
Independent reflections	7188	3659	3521
Observed reflections $I \geq 3\sigma(I)$	4632	3166	3417
Maximum 2 θ (deg)	54	150	150
Ranges <i>h, k, l</i>			
<i>h</i>	-10 to 10	0 to 14	-12 to 0
<i>k</i>	0 to 22	0 to 12	-11 to 0
<i>l</i>	0 to 28	-18 to 18	-21 to 21
Parameters refined	343	172	172
Weighting scheme	unit weight	unit weight	unit weight
(Shift/error) _{max}	0.02	0.01	0.07
Max residual density (e Å ⁻³)	0.667	0.740	0.892
<i>R</i>	0.046	0.077	0.041

mixture which was stirred until dissolution of a solid phase. Then, the layers were separated and the organic phase was washed with 10% hydrochloric acid (10 ml) and water (3 × 10 ml). The organic layer was dried over MgSO₄ and evaporated. Crystallization of the residue from ethyl acetate afforded the pure product **2**, 2.4 g (92%), m.p. 164 °C.

Anal. Found: C, 56.06; H, 4.79. C₁₅H₁₅PS₃ (322.45). Calc.: C, 55.87; H, 4.69%.

¹H NMR: (CH₂)₂, s, δ = 3.19; CH, d, δ = 5.34, ²J_{C-³¹P} = 7.80 Hz, CH_{aromatic}, m, δ = 7.42–7.54, 7.87–7.99. ¹³C NMR: (CH₂)₂, δ = 39.71; CH, δ = 51.72, ¹J_{C-³¹P} = 53.5 Hz, CH_{aromatic}, δ = 128.32, 128.56, 130.63, 131.87, 132.19 132.37. ³¹P NMR: δ = 51.66.

Table 2
Positional parameters with estimated standard deviations for **1**^a

Atom	x	y	z	B (Å ²)
S1	-0.0057(1)	0.15144(6)	0.09438(5)	4.03(2)
S3	-0.0001(1)	0.31816(6)	0.11975(6)	4.74(2)
P1	0.3007(1)	0.22383(5)	0.16359(4)	2.84(2)
O1	0.2611(3)	0.2082(2)	0.2258(1)	4.08(6)
C2	0.1216(4)	0.2367(2)	0.1030(1)	2.78(6)
C5	-0.1244(6)	0.1809(3)	0.1513(2)	6.8(1)
C4	-0.1544(6)	0.2622(3)	0.1482(3)	7.9(1)
C6	0.4141(4)	0.1445(2)	0.1383(2)	2.92(6)
C7	0.4454(5)	0.1397(2)	0.0780(2)	3.86(8)
C8	0.5318(5)	0.0770(3)	0.0607(2)	5.0(1)
C9	0.5856(5)	0.0194(2)	0.1019(2)	5.2(1)
C10	0.5560(5)	0.0240(2)	0.1617(2)	5.3(1)
C11	0.4705(5)	0.0858(2)	0.1800(2)	4.24(8)
C12	0.4190(4)	0.3112(2)	0.1624(2)	3.27(7)
C13	0.4338(5)	0.3511(2)	0.1087(2)	4.24(8)
C14	0.5301(6)	0.4174(3)	0.1118(2)	5.8(1)
C15	0.6115(6)	0.4436(3)	0.1689(3)	6.3(1)
C16	0.5968(5)	0.4054(3)	0.2215(2)	5.6(1)
C17	0.5017(5)	0.3401(3)	0.2188(2)	4.57(9)
S1'	0.5150(2)	0.13323(7)	0.40198(7)	6.26(3)
S3'	0.5345(1)	0.30345(7)	0.39252(5)	5.12(2)
P1'	0.2219(1)	0.22981(5)	0.41166(4)	3.03(2)
O1'	0.2615(3)	0.2316(2)	0.4802(1)	4.13(6)
C2'	0.4013(4)	0.2193(2)	0.3751(2)	3.69(7)
C5'	0.6525(6)	0.1810(4)	0.4626(3)	8.0(2)
C4'	0.6991(6)	0.2546(4)	0.4419(3)	8.2(2)
C6'	0.0906(4)	0.1495(2)	0.3858(2)	3.35(7)
C7'	0.0166(7)	0.1389(3)	0.3250(2)	6.6(1)
C8'	-0.0892(7)	0.0773(3)	0.3082(2)	7.4(1)
C9'	-0.1197(6)	0.0252(3)	0.3499(2)	5.5(1)
C10'	-0.0447(7)	0.0337(3)	0.4091(2)	7.3(1)
C11'	0.0600(6)	0.0950(3)	0.4276(2)	6.1(1)
C12'	0.1228(4)	0.3172(2)	0.3805(2)	3.27(7)
C13'	0.1096(5)	0.3383(2)	0.3180(2)	4.04(8)
C14'	0.0312(6)	0.4062(3)	0.2971(2)	5.2(1)
C15'	-0.0355(5)	0.4539(3)	0.3361(2)	5.7(1)
C16'	-0.0217(5)	0.4343(3)	0.3975(2)	5.6(1)
C17'	0.0574(5)	0.3664(2)	0.4196(2)	4.43(9)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 3
Positional parameters with estimated standard deviations for **2**^a

Atom	x	y	z	B (Å ²)
S2	0.6988(1)	0.0688(2)	0.3384(1)	3.80(3)
S1	0.5398(1)	0.1644(2)	0.0625(2)	5.09(4)
S3	0.6372(1)	0.4048(2)	0.1755(2)	5.45(4)
P1	0.73474(9)	0.1344(1)	0.1879(1)	2.67(2)
C2	0.6501(3)	0.2455(6)	0.0986(5)	3.2(1)
C5	0.4865(5)	0.254(1)	0.177(1)	9.5(3)
C4	0.5217(6)	0.393(1)	0.193(1)	8.3(3)
C6	0.7542(4)	-0.0032(6)	0.0857(5)	3.0(1)
C7	0.7246(5)	-0.1331(6)	0.1077(6)	4.3(1)
C8	0.7428(5)	-0.2391(7)	0.0315(7)	5.5(2)
C9	0.7896(5)	-0.2149(7)	-0.0650(6)	5.0(2)
C10	0.8172(6)	-0.0878(8)	-0.0870(7)	6.0(2)
C11	0.8014(5)	0.0198(7)	-0.0112(6)	5.3(2)
C12	0.8409(3)	0.2323(6)	0.2112(5)	3.1(1)
C13	0.8604(4)	0.3349(7)	0.1329(6)	4.5(1)
C14	0.9422(5)	0.4042(8)	0.1533(7)	5.8(2)
C15	1.0070(5)	0.3739(9)	0.2508(8)	6.4(2)
C16	0.9876(5)	0.2774(9)	0.3306(8)	6.1(2)
C17	0.9050(4)	0.2056(7)	0.3123(6)	4.4(1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

2.3. 2-Diphenylselenophosphinoyl-1,3-dithiolane **3**

To a solution of the phosphine sulphide **2** (1.246 g, 0.00387 mol) in methylene chloride (40 ml) methyl triflate (0.46 ml) was added under nitrogen. The reaction mixture was refluxed for 1 h and cooled to 0 °C. Tris(dimethylamino)phosphine (0.76 ml) was added dropwise at this temperature for 5 min and then selenium (0.41 g) added. The reaction mixture was stirred for 3 h, washed with water (2 × 20 ml), dried over MgSO₄ and evaporated. The solid residue was extracted with benzene (10 × 10 ml). Evaporation of the solvent gave the crude product **3** which was crystallized from a mixture of chloroform and pentane, 0.57 g (68%), m.p. 126 °C.

Anal. Found: C, 48.99; H, 4.07. C₁₅H₁₅PS₂Se (369.35). Calc.: C, 48.78; H, 4.09%.

¹H NMR: (CH₂)₂, m, δ = 3.11; CH, d, δ = 5.0, ²J_{H-³¹P} = 7.80 Hz, CH_{aromatic}, m, δ = 7.39–7.51, 7.70–7.96. ¹³C NMR: (CH₂)₂, δ = 38.64; CH, δ = 51.5, ¹J_{C-³¹P} = 44.1 Hz, CH_{aromatic}, δ = 128.18, 128.29, 129.40, 131.78, 131.84, 132.66. ³¹P NMR: δ = 46.55, ¹J_{Se-³¹P} = 750 Hz.

2.4. Crystal structures of **1–3**

Crystal and molecular structures of **1–3** were determined using data collected at room temperature on a CAD4 diffractometer with graphite monochromatized radiation [5]. The dithiolanes **1** and **2** crystallize in the monoclinic system, and only **3** is orthorhombic. Lattice constants were refined by least squares fit of 25 reflec-

Table 4
Positional parameters with estimated standard deviations for **3**^a

Atom	x	y	z	B (Å ²)
Se1	0.68746(8)	0.20538(7)	0.37887(4)	4.87(1)
S1	0.5840(1)	-0.0741(2)	0.22949(8)	3.92(3)
S3	0.8101(2)	0.1011(2)	0.16887(8)	4.19(3)
P1	0.8003(1)	0.0291(1)	0.33944(7)	2.86(2)
C2	0.7620(5)	-0.0300(6)	0.2406(3)	3.01(9)
C5	0.5385(7)	0.0871(9)	0.1840(4)	8.4(2)
C4	0.6373(7)	0.1396(9)	0.1337(4)	7.4(2)
C6	0.7699(5)	-0.1353(6)	0.3933(3)	3.2(1)
C7	0.8463(6)	-0.2567(6)	0.3769(4)	4.5(1)
C8	0.8207(8)	-0.3846(7)	0.4170(4)	5.6(1)
C9	0.7151(7)	-0.3894(7)	0.4707(3)	5.8(1)
C10	0.6399(8)	-0.2696(8)	0.4860(3)	6.0(2)
C11	0.6653(6)	-0.1413(7)	0.4489(3)	4.5(1)
C12	0.9841(5)	0.0589(5)	0.3402(3)	3.06(9)
C13	1.0349(6)	0.1620(6)	0.3898(3)	4.0(1)
C14	1.1742(7)	0.1852(6)	0.3927(3)	5.0(1)
C15	1.2618(6)	0.1032(7)	0.3463(3)	5.1(1)
C16	1.2100(6)	0.0029(7)	0.2973(3)	4.6(1)
C17	1.0689(5)	-0.0201(6)	0.2940(3)	3.8(1)

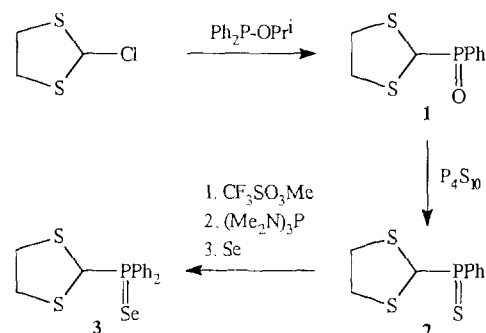
^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

tions in the θ ranges 8.5–15.7° for **1**, 20.7–27.7° for **2**, and 7.1–27.1° for **3**. Crystal data and experimental details are shown in Table 1, and atom coordinates in Tables 2–4.

For compounds **2** and **3**, an empirical absorption correction was applied using the ψ -scan method [6,7]. All structures were solved by direct methods and refined by full matrix least squares using F [6,8]. Hydrogen atoms were placed geometrically at idealized positions and set as riding, with fixed isotropic thermal parameters equal to $B_{\text{iso}} = 4.0 \text{ \AA}^2$. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All calculations were carried out with the Enraf–Nonius SDP crystallographic computing package [6] except first structure solutions by the xs program [9]. Further details of the crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.²

3. Results and discussion

The desired dithiolanes **1–3** were prepared as shown in Scheme 1. The Arbuzov reaction of 2-chloro-1,3-dithiolane, prepared in situ from 1,3-dithiolane and *N*-chlorosuccinimide, with isopropyl diphenylphosphinite gave 2-diphenylphosphinoyl-1,3-dithiolane **1** isolated in a pure state by crystallization from ethyl acetate in 57%



Scheme 1. Synthesis of 2-Ph₂P=X (X = O, S, Se) substituted 1,3-dithiolanes **1–3**.

yield. The conversion of the latter to its thiophosphoryl analogue **2** was carried out by refluxing **1** with phosphorus pentasulphide in a benzene solution. The dithiolane **2** was purified by crystallization from ethyl acetate and obtained in 92% yield. Finally, 2-selenophosphoryl-1,3-dithiolane **3** was synthesized from **2** in a one-pot reaction involving three consecutive steps [10]. In the first step, the thiophosphoryl sulphur atom was methylated by methyl triflate to give the corresponding *S*-methyl phosphonium salt. Then, this salt was converted into diphenyl-2(1,3-dithiolanyl)phosphine upon treatment with hexamethyl phosphorus triamide. Finally, addition of elemental selenium to the phosphine formed gave the desired dithiolane **3** as a crystalline compound isolated in 68% yield by crystallization from chloroform–pentane.

Three-dimensional views of the structures of the dithiolanes **1–3** with the atom numbering are shown in Figs. 1–3 respectively. Interestingly, the phosphoryl dithiolane **1** exists in the crystal as a dyad in which two molecules of **1** are connected by an intermolecular hydrogen bond $\text{H}(\text{C}2) \cdots \text{O}=\text{P} <$, with $\text{H}(\text{C}2) \cdots \text{O}1$ distance of 2.352 Å and $\text{H}(\text{C}2) \cdots \text{O}1-\text{P}1$ angle of

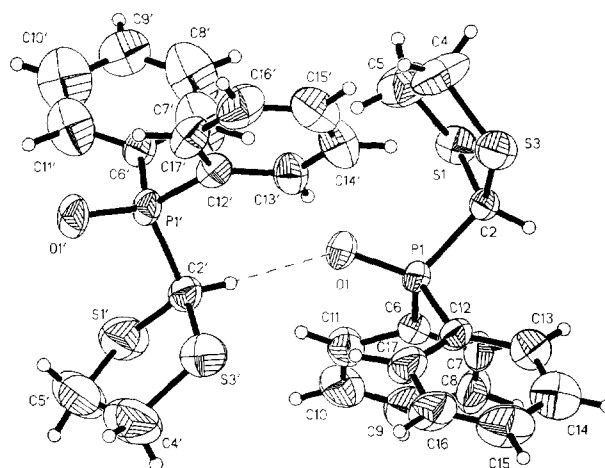


Fig. 1. Ellipsoidal view of two independent molecules in an asymmetric part of the unit cell of **1**. Displacement ellipsoids are shown with 50% probability.

² Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

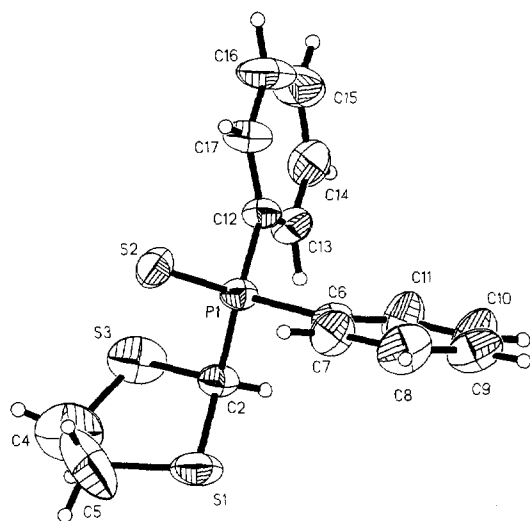


Fig. 2. Ellipsoidal view of the molecule of **2**. Displacement ellipsoids are shown with 50% probability.

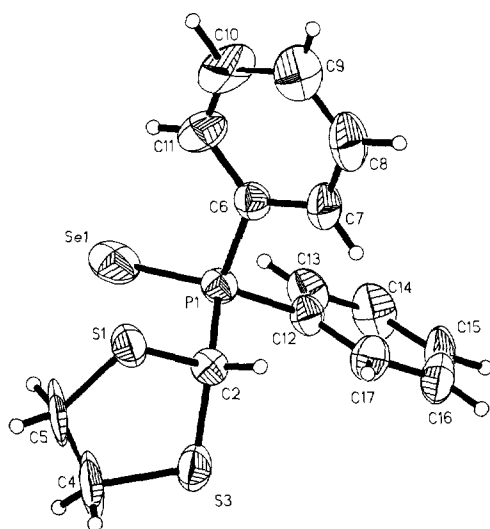


Fig. 3. Ellipsoidal view of the molecule of **3**. Displacement ellipsoids are shown with 50% probability.

Table 5
Selected bond distances (Å) in compounds **1–3**

	1 (X = O)		2 (X = S)	3 (X = Se)
	mol. 1	mol. 2		
P1–X	1.493(2)	1.490(2)	1.953(2)	2.102(1)
P1–C2	1.827(3)	1.821(4)	1.833(5)	1.844(5)
C2–S1	1.801(3)	1.803(4)	1.793(5)	1.809(6)
C2–S3	1.808(3)	1.824(4)	1.806(7)	1.813(6)
S1–C5	1.790(5)	1.797(6)	1.83(1)	1.760(9)
S3–C4	1.802(6)	1.798(5)	1.74(1)	1.842(7)
C4–C5	1.427(8)	1.426(9)	1.45(1)	1.40(2)
P1–C6	1.804(3)	1.792(4)	1.819(6)	1.825(5)
P1–C12	1.802(4)	1.795(3)	1.814(5)	1.829(5)

Table 6
Selected valence angles (deg) in compounds **1–3**

	1 (X = O)		2 (X = S)	3 (X = Se)
	mol. 1	mol. 2		
X–P1–C2	114.5(1)	113.7(1)	115.1(3)	115.5(2)
P1–C2–S1	111.3(2)	111.0(3)	112.1(4)	111.5(3)
P1–C2–S3	110.8(2)	109.8(2)	111.3(3)	112.7(3)
S1–C2–S3	108.6(2)	109.0(2)	109.7(3)	109.5(3)
C2–S1–C5	94.3(3)	95.3(2)	95.4(3)	95.7(3)
S1–C5–C4	111.4(4)	110.0(4)	111.0(7)	113.9(5)
C5–C4–S3	114.0(4)	113.1(4)	112.6(7)	111.4(5)
C4–S3–C2	96.4(2)	96.9(2)	99.6(4)	97.0(3)
C2–P1–C6	105.4(4)	106.3(2)	104.7(3)	101.1(2)
C2–P1–C12	105.2(4)	105.5(2)	105.2(2)	104.8(2)
X–P1–C6	111.0(2)	110.6(2)	112.2(2)	114.0(2)
C6–P1–C12	108.5(2)	108.5(2)	105.8(3)	106.7(2)
X–P1–C12	111.9(2)	112.1(2)	113.0(2)	113.6(2)

Table 7
Distances of axial hydrogen atoms H(C4) and H(C5) from the X atom (X = O, S, Se) in compounds **1–3**

	1 (X = O)		2 (X = S)	3 (X = Se)
	mol. 1	mol. 2		
X–H(C4)	3.686	4.080	4.431	4.414
X–H(C5)	2.729	2.844	3.198	3.179

Table 8
Conformation of the molecules of **1–3**: selected torsion angles (deg) and asymmetry parameters of 1,3-dithiolane rings

	1 (X = O)		2 (X = S, Y = C5)	3 (X = Se, Y = C5)
	mol. 1 (Y = S1)	mol. 2 (Y = C5)		
CS–S1–C2–S3	–34.4(2)	27.8(2)	–21.8(5)	–24.3(3)
S1–C2–S3–C4	21.7(2)	–11.1(2)	6.5(5)	9.2(3)
C2–S3–C4–C5	3.9(4)	–16.1(4)	17.1(8)	14.5(6)
S3–C4–C5–S1	–28.7(5)	37.7(5)	–35.0(10)	–34.7(7)
C4–C5–S1–C2	38.7(4)	–40.1(4)	34.3(7)	37.0(6)
C4–S3–C2–P1	–100.8(2)	110.6(2)	–118.0(4)	–115.4(3)
C5–S1–C2–P1	87.8(2)	–93.2(2)	102.3(4)	101.1(4)
X–P1–C2–S1	–60.2(2)	56.9(2)	–56.4(3)	–57.1(3)
X–P1–C2–S3	60.7(2)	–63.7(2)	66.8(3)	66.4(3)
ΔC_s (Y)	5.8(1)	8.5(1)	3.3(1)	7.1(1)
ΔC_2 (S1–C5)	13.2(1)	7.9(1)	11.7(1)	8.2(1)

Table 9
Dihedral angles between important least-squares planes (deg) in compounds 1–3

Planes	1 (X = O)		2 (X = S)		3 (X = Se)	
	mol. 1	mol. 2				
S1,C2,S3,C4,C5/ /X,P1,C2	87.1(1)	94.6(2)	84.2(2)	96.2(2)		
S1,C2,S3,C4,C5/ /C6,C7,C8,C9,C10,C11	55.1(2)	40.3(2)	40.8(4)	47.9(2)		
S1,C2,S3,C4,C5/ /C12,C13,C14,C15,C16,C17	110.9(1)	109.1(1)	89.9(2)	85.6(1)		
C6,C7,C8,C9,C10,C11/ /C12,C13,C14,C15,C16,C17	112.0(1)	112.5(1)	102.2(2)	67.3(2)		

143.8°. Therefore, they differ slightly in structural parameters. Selected important bond lengths and valence angles in 1–3 are collected in Tables 5 and 6.

It was found that the investigated compounds 1–3 exist in a twist (T) conformation with the phosphorus atom situated in the pseudoaxial position. The heteroatom X (X = O, S, Se) is placed over the 1,3-dithiolane ring and it is directed towards this endocyclic sulphur atom S1 which is located closer to the anomeric carbon atom. The distances between the pseudoaxial hydrogens at the carbon atoms C4 and C5 and the heteroatom X are collected in Table 7.

Asymmetry parameters of the three five-membered heterocyclic rings, calculated from the values of the torsion angles [11], are given in Table 8. The most deviated ring atom from the least-squares plane of the five-membered ring in the molecule of 1 is the sulphur atom S1, while in compounds 2 and 3 it is the carbon atom C5. The other interesting data defining the conformation of the investigated dithiolanes 1–3 are in Table 9 which lists the dihedral angles between important least-squares planes.

The most important finding of the present study is that in the solid state conformation of the dithiolanes 1–3 the Ph₂P=X group is pseudoaxial irrespective of the nature of heteroatom X (O, S, Se). A comparison of bond distances in the five-membered rings reveals interesting differences. In the case of the dithiolanes 1 and 2 one observes a shortening of the endocyclic S1–C2 bond compared with the corresponding S3–C2 bond (0.021 Å and 0.013 Å respectively). This difference in

the dithiolane 3 is rather small. Moreover, such a shortening of the S1–C2 bond is characteristic for the sulphur atom which is more distant from the ring plane. The other important conformational differences are reflected in the different values of the valence angles C2–S3–C4 and C2–S1–C5. It can be distinctly seen from Table 6 that the values of the latter angles in all compounds examined are smaller. Finally, it was also found that the distances between the pseudoaxial C4 and C5 hydrogens and the heteroatom X are not equal. Interestingly, the shorter H···O=P distance for 1 of 2.73 Å is almost equal to the sum of the H and O van der Waals radii (H = 1.20 Å, O = 1.50 Å), thus suggesting the formation of an H···O hydrogen bond [12].

Assuming that crystal packing forces are not so important as intramolecular interactions, the X-ray structural data discussed above support the view that the n_S → σ_{C–P}^{*} negative hyperconjugation with the sulphur atom S1 as a more effective donor is one of the factors responsible for the anomeric effect operating in 2-Ph₂P=X substituted 1,3-dithiolanes.

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