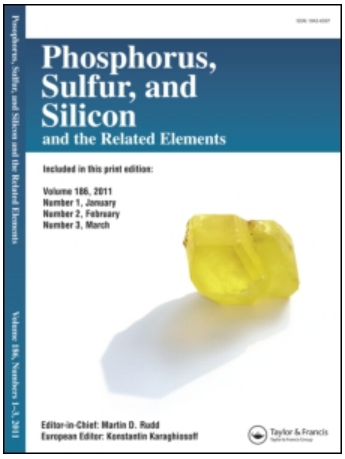

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MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF 2-0-[BIS(DIETHYLAMIDO)THIONOPHOSPHATE]-3,4-0,0-(DIETHYLAMIDOTHIONOPHOSPHATE)-1,6-ANHYDRO-β-D-GLUCOPYRANOSE

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MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF 2-0-[BIS(DIETHYLAMIDO)THIONOPHOSPHATE]-3,4-0,0-(DIETHYLAMIDOTHIONOPHOSPHATE)-1,6-ANHYDRO-β-D-GLUCOPYRANOSE

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The crystal and molecular structure of 2-0-[bis(diethylamido)thionophosphate]-3,4-0,0-(diethylamidothionophosphate)-1,6-anhydro-β-D-glucopyranose, $C_{18}H_{37}N_3P_2O_5S_2$, and its absolute configuration have been determined by an X-ray study. The pyranose ring has a twist-boat conformation; both five-membered rings are in a twisted envelope conformation. A considerable dispersion of the C—C bond lengths in the pyranose ring can be attributed to its strong conformational distortion.

According to an X-ray structure analysis, PCl_3 and $P(OMe)_3$ react only with the thermodynamically less stable chair-conformers $^1C_4$ of methyl-α- and methyl-β-D-ribopyranose, having axial orientations of 1- and 3- hydroxy groups.[1] The pyranose ring in products of this reaction and their thioadducts possess a distorted chair conformation.[1]

Both methyl-β-D-ribopyranose and 1,6-anhydro-β-D-glucopyranose **1** have the $^1C_4$ conformation with axial hydroxy groups at C(2) and C(4), but the C(3) configuration in these molecules is different.[2,3] We studied the reaction of **1** with $P(NEt_2)_3$ and sulfur which yielded dithionodiphosphate, $C_{18}H_{37}N_3P_2O_5S_2$, **2** (m.p. 77°C), isolated by chromatography. On the basis of the ^{31}P n.m.r. spectrum it was concluded that **2** contained a dioxaphospholane ring ($\delta_{31P} = -89$ p.p.m.). In order to elucidate a possible conformational change of the pyranose ring in **2** and to determine details of its molecular structure, we have undertaken the present X-ray study.

EXPERIMENTAL

Crystals of **2** are orthorhombic, a = 11.371(1), b = 25.047(4), c = 9.3215(5) Å, d_{calc} = 1.25 g/ccm, Z = 4, space group $P\,2_12_12_1$.

Cell parameters and intensities of 2174 independent reflections with $F_2 > 2\sigma$ were measured with an automated four-circle Hilger and Watts diffractometer. Data were collected at room temperature with graphite monochromated CuK α radiation (λ = 1.54178 Å) using Θ/2Θ-scan up to Θ = 66°.

The structure was determined by the MULTAN procedure and refined by full-matrix least-squares first in isotropic approximation. Hydrogen atoms positions were obtained from a difference map. The contribution of hydrogen atoms was included in the final least-squares cycles with $B_{iso} = 5.0$ Å^2, but

their parameters were not refined. The final anisotropic refinement of non-hydrogen atoms then gave convergence to the conventional R- factor of 0.051, and R_w being 0.049.

The absolute configuration was determined taking into account anomalous scattering by P and S atoms. The refinement of the enantiomeric (inverted) structure converged to R = 0.057, and R_w = 0.055 and therefore this enantiomer could be rejected at the 0.005 significance level. The absolute configuration found was also confirmed by least squares determination of $\Delta f''$ parameters[4] for P and S atoms in the enantiomeric structure with the lower residual, starting $\Delta f''$ values being set to zero. The final values of $\Delta f''_p = 0.34(4)$ and $\Delta f''_s = 0.50(5)$, are positive and in a good agreement with those tabulated[5] for CuKα radiation, viz. $\Delta f''_p = 0.43$ and $\Delta f''_s = 0.56$.

All calculations were performed with an ECLIPSE S/200—computer using modified† EXTL—program package.

Atomic positional and thermal parameters are given in Table I, the molecular structure is illustrated in the Figure, bond lengths and angles and torsion angles are listed in Tables II, III and IV respectively.

TABLE I

Atomic coordinates ($\times 10^4$) with anisotropic temperature factors in the form:
$T=\exp[-1/4(B_{11}a^{*2}h^2+B_{22}b^{*2}k^2+B_{33}c^{*2}1^2+2B_{12}a^*b^*hk+2B_{13}a^*c^*hl+2B_{23}b^*c^*kl)]$.

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P(1)	−5245(1)	−4001(1)	−638(2)	4.11(7)	3.37(6)	4.15(8)	0.54(6)	−0.37(7)	−0.22(6)
P(2)	−4162(1)	−6254(1)	−1576(2)	4.13(7)	2.85(6)	4.15(7)	−0.35(6)	0.08(7)	−0.21(6)
S(1)	−5688(2)	−4042(1)	−2634(2)	7.0(1)	7.1(1)	4.68(9)	1.5(1)	−1.34(9)	−0.32(8)
S(2)	−4396(2)	−6507(1)	−3495(2)	6.07(9)	5.00(8)	4.17(8)	−1.08(7)	0.10(8)	0.77(7)
O(1)	−1552(4)	−4607(1)	−1895(4)	4.5(2)	3.8(2)	3.0(2)	−0.5(2)	0.7(2)	0.4(1)
O(2)	−4384(3)	−4479(1)	−143(4)	4.8(2)	3.0(2)	3.0(2)	1.0(2)	0.1(2)	0.3(1)
O(3)	−4604(3)	−5645(1)	−1309(4)	3.4(2)	2.5(2)	4.9(2)	−0.2(1)	0.4(2)	0.0(1)
O(4)	−2806(3)	−6167(1)	−1091(4)	3.8(2)	2.5(2)	4.4(2)	0.3(1)	0.0(2)	0.1(1)
O5)	−1825(3)	−4946(1)	351(4)	4.5(2)	3.4(2)	2.8(2)	−0.4(2)	−0.1(2)	−0.1(1)
N(1)	−4592(5)	−3445(2)	−201(6)	5.0(3)	2.5(2)	5.1(3)	0.0(2)	−0.9(2)	0.5(2)
N(2)	−6237(4)	−4092(2)	610(6)	4.3(3)	4.7(3)	5.6(3)	0.0(2)	1.1(2)	−1.1(3)
N(3)	−4765(5)	−6619(2)	−340(5)	5.7(2)	2.9(2)	3.6(2)	−1.2(2)	0.1(2)	−0.1(2)
C(1)	−2301(5)	−4580(2)	−661(6)	4.8(4)	2.9(2)	3.0(3)	−0.4(2)	0.3(3)	−0.1(2)
C(2)	−3576(5)	−4748(2)	−1077(6)	4.2(3)	2.2(2)	2.7(2)	0.0(2)	0.4(2)	0.0(2)
C(3)	−3626(5)	−5335(2)	−719(6)	3.5(3)	2.5(2)	3.5(3)	0.2(2)	0.3(2)	0.0(2)
C(4)	−2523(5)	−5603(2)	−1348(6)	3.9(3)	2.4(2)	3.4(3)	0.0(2)	0.3(2)	−0.1(2)
C(5)	−1447(5)	−5381(2)	−603(6)	3.6(3)	3.6(3)	3.3(3)	−0.1(2)	−0.4(2)	−0.2(2)
C(6)	−766(5)	−5052(2)	−1660(7)	3.5(3)	5.0(3)	4.5(3)	−0.8(3)	0.0(3)	−0.5(3)
C(7)	−4229(8)	−3055(3)	−1301(9)	6.9(5)	4.3(3)	7.8(5)	1.1(3)	−0.6(4)	1.9(3)
C(8)	−3030(9)	−3128(4)	−1843(12)	7.8(5)	10.7(6)	11.7(7)	0.9(5)	2.3(6)	7.4(6)
C(9)	−4022(6)	−3411(2)	1212(8)	5.2(4)	4.2(3)	5.5(4)	−0.7(3)	−0.4(3)	−1.2(3)
C(10)	−4156(9)	−2865(3)	1910(11)	11.1(6)	6.6(4)	10.9(7)	1.5(5)	0.0(6)	−4.4(5)
C(11)	−7018(7)	−3656(4)	1045(11)	4.9(4)	9.0(6)	10.7(7)	0.5(4)	2.2(4)	−2.9(5)
C(12)	−7283(9)	−3633(5)	2581(13)	8.4(6)	14.1(9)	11.9(8)	0.3(6)	2.4(6)	−7.0(7)
C(13)	−6728(6)	−4635(3)	868(9)	4.5(4)	7.5(4)	7.7(5)	−1.0(3)	0.3(4)	0.8(4)
C(14)	−7828(10)	−4745(4)	107(13)	10.4(7)	9.0(6)	11.8(7)	−2.7(6)	−3.3(6)	1.6(6)
C(15)	−4793(7)	−6442(3)	1160(7)	7.5(4)	4.0(3)	4.4(3)	−1.0(3)	0.7(3)	0.0(3)
C(16)	−5950(9)	−6266(4)	1630(11)	10.2(6)	9.1(5)	7.5(5)	1.3(5)	3.6(5)	−0.4(5)
C(17)	−5105(7)	−7177(2)	−610(8)	6.9(4)	3.1(3)	6.0(4)	−1.6(3)	−1.6(4)	0.2(3)
C(18)	−4098(9)	−7556(3)	−411(10)	12.7(7)	4.5(3)	7.4(5)	0.9(4)	−1.9(6)	−0.5(4)

† These programs were modified in the X-Ray Laboratory of the Institute of Organo-Element Compounds by A. I. Yanovsky and R. G. Gerr.

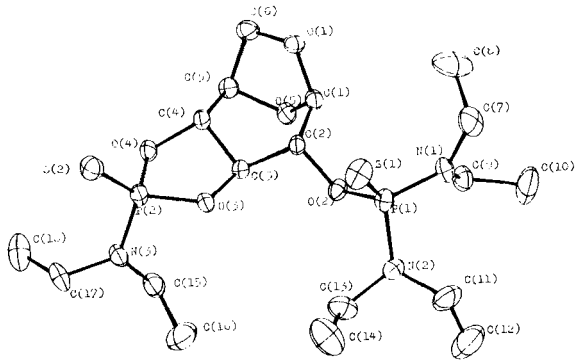

FIGURE 1 Structural parameters of **2.**

TABLE II

Bond lengths (d, Å)

Bond	d	Bond	d
C(1)—C(2)	1.558(8)	N(1)—C(7)	1.475(9)
C(2)—C(3)	1.509(7)	N(1)—C(9)	1.470(9)
C(3)—C(4)	1.539(8)	C(7)—C(8)	1.46(1)
C(4)—C(5)	1.514(8)	C(9)—C(10)	1.52(1)
C(5)—C(6)	1.500(8)	N(2)—C(11)	1.46(1)
C(1)—O(1)	1.433(7)	N(2)—C(13)	1.491(9)
C(6)—O(1)	1.445(7)	C(11)—C(12)	1.46(2)
C(2)—O(2)	1.433(7)	C(13)—C(14)	1.46(1)
C(3)—O(3)	1.464(7)	P(2)—S(2)	1.916(2)
C(4)—O(4)	1.468(6)	P(2)—O(3)	1.624(4)
C(5)—O(5)	1.470(7)	P(2)—O(4)	1.621(4)
C(1)—O(5)	1.422(7)	P(2)—N(3)	1.623(5)
P(1)—S(1)	1.930(3)	N(3)—C(15)	1.467(8)
P(1)—O(2)	1.614(4)	N(3)—C(17)	1.472(7)
P(1)—N(1)	1.639(5)	C(15)—C(16)	1.46(1)
P(1)—N(2)	1.637(6)	C(17)—C(18)	1.50(1)

TABLE III

Bond angles (ω, °).

Angle	ω	Angle	ω	Angle	ω
S(1)P(1)O(2)	113.2(2)	C(1)O(5)C(5)	100.8(4)	O(3)C(3)C(2)	117.6(4)
S(1)P(1)N(1)	114.0(2)	P(1)N(1)C(7)	121.2(4)	O(3)C(3)C(4)	104.1(4)
S(1)P(1)N(2)	119.8(2)	P(1)N(1)N(9)	118.3(4)	C(2)C(3)C(4)	108.1(4)
O(2)P(1)N(1)	106.6(2)	C(7)N(1)C(9)	117.5(5)	O(4)C(4)C(3)	100.3(4)
O(2)P(1)N(2)	96.4(2)	P(1)N(2)C(11)	120.8(5)	O(4)C(4)C(5)	117.2(4)
N(1)P(1)N(2)	104.8(3)	P(1)N(2)C(13)	120.0(5)	C(3)C(4)C(5)	108.8(4)
S(2)P(2)O(3)	114.3(2)	C(11)N(2)C(13)	114.1(6)	O(5)C(5)C(4)	108.3(4)
S(2)P(2)O(4)	115.9(2)	P(2)N(3)C(15)	121.1(4)	O(5)C(5)C(6)	98.1(4)
S(2)P(2)N(3)	114.6(2)	P(2)N(3)C(17)	121.7(4)	C(4)C(5)C(6)	108.6(5)
O(3)P(2)O(4)	97.3(2)	C(15)N(3)C(17)	116.3(5)	O(1)C(6)C(5)	101.8(5)
O(3)P(2)N(3)	106.8(2)	O(1)C(1)O(5)	106.0(4)	N(1)C(7)C(8)	114.7(7)
O(4)P(2)N(3)	106.2(2)	O(1)C(1)C(2)	110.0(4)	N(1)C(9)C(10)	113.0(6)
C(1)O(1)C(6)	106.4(4)	O(5)C(1)C(2)	110.2(4)	N(2)C(11)C(12)	115.2(8)
P(1)O(2)C(2)	124.3(3)	O(2)C(2)C(1)	109.6(4)	N(2)C(13)C(14)	114.4(7)
P(2)O(3)C(3)	108.7(3)	O(2)C(2)C(3)	107.4(4)	N(3)C(15)C(16)	113.5(6)
P(2)O(4)C(4)	106.9(3)	C(1)C(2)C(3)	104.0(4)	N(3)C(17)C(18)	112.3(6)

TABLE IV

Torsion Angles (τ, °).

Angle	τ	Angle	τ
C(1)—C(2)—C(3)—C(4)	−47.7(6)	O(4)—C(4)—C(3)—O(3)	−46.3(5)
C(2)—C(3)—C(4)—C(5)	64.4(6)	C(4)—C(3)—O(3)—P(2)	29.6(4)
C(3)—C(4)—C(5)—O(5)	−5.9(5)		
C(4)—C(5)—O(5)—C(1)	−62.3(6)	C(1)—O(5)—C(5)—C(6)	50.5(7)
C(5)—O(5)—C(1)—C(2)	81.2(6)	O(5)—C(5)—C(6)—O(1)	−44.7(6)
O(5)—C(1)—C(2)—C(3)	−22.0(5)	C(5)—C(6)—O(1)—C(1)	22.8(6)
		C(6)—O(1)—C(1)—O(5)	9.1(6)
C(3)—O(3)—P(2)—O(4)	−2.6(5)	O(1)—C(1)—O(5)—C(5)	−37.8(6)
O(3)—P(2)—O(4)—C(4)	−26.9(5)		
P(2)—O(4)—C(4)—C(3)	45.3(5)	O(4)—C(4)—C(5)—C(6)	135.7(8)
		C(3)—C(2)—C(1)—O(1)	94.5(6)

DISCUSSION

Unlike initial 1,6-anhydro-β-D-glucopyranose **1**,[3] the pyranose ring C(1)C(2)C(3)C(4)C(5)O(5) in the molecule **2** exhibits a twist-boat conformation. The atoms C(1), C(2), C(4), C(5) are not coplanar, the deviations of C(1) and C(4) from the best plane through C(1)C(2)C(4)C(5) being 0.085 and 0.078 Å, and those of C(2) and C(5) being −0.077 and −0.086 Å, respectively. The distances of O(5) and C(3) from this plane are −0.85 and −0.71 Å, O(2) and O(4) bonded to C(2) and C(4), respectively, lie on the other side of this plane at the distances of 0.54 and 1.02 Å. The O(3) deviation from the C(2)C(3)C(4) plane is 1.15 Å. Both five-membered cycles C(1)O(5)C(2)C(6)O(1) and P(2)O(3)C(3)C(4)O(4) are in a somewhat twisted envelope conformation.

Both P-atoms have tetrahedral co-ordination. The bond lengths P(2)—O(3) and P(2)—O(4) (av. 1.623(2) Å) are slightly increased in comparison with P—O bonds in previously studied related heterocyclic phosphorus compounds (1.58–1.61 Å),[6,7] including such bonds in dioxaphospholane rings (1.585(7)–1.608(4) Å).[8,9] The bond lengths P(1)—S(1) of 1.930(3) Å and P(2)—S(2) of 1.916(2) Å are also longer than the standard value of 1.884(2) Å for the P=S double bond.[1] The P—N bond lengths (av. 1.633(3) Å) fall into the interval of 1.62–1.64 Å, typical for such bonds.[6] The nitrogen atoms N(1), N(2) and N(3) have almost planar coordination (sums of bond angles are 357, 355 and 359° respectively). The C—N bond lengths cover the

TABLE V

Comparison of bond lengths (Å) the anhydro-β-D-glucopyranose rings of the molecules **1** and **2**.

Bond	**1**[1]	**2** this work
C(1)—C(2)	1.518(4)	1.558(8)
C(2)—C(3)	1.537(4)	1.509(7)
C(3)—C(4)	1.540(4)	1.539(8)
C(4)—C(5)	1.516(5)	1.514(8)
C(5)—O(5)	1.443(4)	1.470(7)
O(5)—C(1)	1.399(4)	1.422(7)
C(5)—C(6)	1.527(5)	1.500(8)
C(6)—O(1)	1.444(4)	1.445(7)
O(1)—C(1)	1.427(4)	1.433(7)

range of 1.46–1.49 Å, i.e. they do not differ significantly from the standard length of the C(sp^3)—N bonds.

A considerable difference between lengths of similar bonds in the pyranose ring of molecules (1) and (2) (see Table V) can be attributed to a strong conformational distortion of this ring. The bond lengths of the same type in the dioxaphospholane cycle are equal within the limits of our accuracy. The endocyclic angle O(3)P(2)O(4) is 97.3(2)°, and falls into the interval of 93.6–100.8° typical for these heterocycles.[1,6] In both five-membered rings, endocyclic angles at C atoms are as usual decreased (av. 102.1(2)°).[1,6,8,9]

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