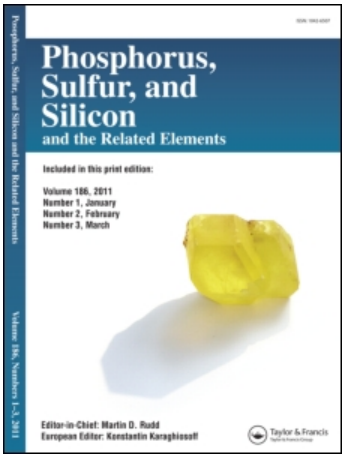

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MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF 2-[1',2'; 3',4'-BIS-O-(N-DIMETHYLAMIDOTHIONOPHOSPHATE)-D-ARABINOTETRAOXYBUTYL]QUINOXALINE

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MOLECULAR STRUCTURE AND ABSOLUTE CONFIGURATION OF 2-[1′,2′; 3′,4′-BIS-O-(N-DIMETHYLAMIDOTHIONOPHOSPHATE)-D-ARABINOTETRAOXYBUTYL]QUINOXALINE

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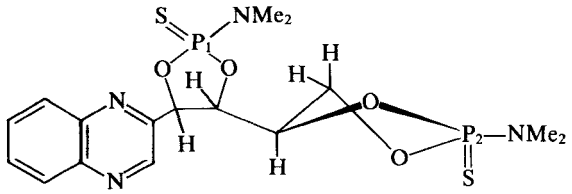
The crystal and molecular structure of 2-[1′,2′;3′,4′-bis-O-(N-dimethylamidothionophosphate)-D-arabinotetraoxybutyl]quinoxaline, $C_{16}H_{21}N_4P_2S_2O_4$, and its absolute configuration have been determined by an X-ray study. One of the dioxaphospholane rings has an envelope conformation, the other is in a twist conformation. The quinoxaline ring is planar.

The reaction of 2-[D-arabinotetrahydroxybutyl]quinoxaline with $P(NMe_2)_3$ and sulfur afforded a compound, $C_{16}H_{21}N_4P_2S_2O_4$, (**1**) (m.p. 205–206°C) isolated by chromatography on silica. On the basis of PMR-data the following structure of (**1**) was proposed:



1

In order to confirm this structure and to establish details of the stereochemistry of (**1**) its X-ray structure analysis was undertaken.

EXPERIMENTAL

Crystals of (1) are orthorhombic, a = 23.843(3), b = 10.843(1), c = 8.3227(6) Å, d_{calc} = 142g/cm^3, Z = 4, space group $P2_12_12_1$.

Cell parameters and intensities of 1362 independent reflections with $F^2 > 2\sigma$ were measured with an automated four-circle Hilger and Watts diffractometer (λCuK_α, $\Theta/2\Theta$-scan, $\Theta \leq 66°$, graphite monochromator).

The structure was determinated by direct methods using the MULTAN program and refined by full-matrix least-squares with isotropic temperature factors. Positions of ring H atoms were calculated and those of hydrogens of methyl groups were obtained from a difference map. H atoms contributions were taken into account in the final least-squares cycles, though their positions and thermal parameters (B_{iso} = 5 Å^2) were not refined. The refinement converged to the conventional R factor of 0.0702 (weighted R_w = 0.0735). The absolute configuration was determined taking into account anomalous scattering by P and S atoms. The refinement of enantiomeric (inverted) structure converged to the R fac-

tor of 0.0751, ($R_w = 0.0772$), and could be rejected at the 0.005 significance level. The independent confirmation of the absolute configuration was obtained according to[1] by including $\Delta f''$ parameters for P and S atoms into refinement of the model with lower residuals (starting $\Delta f''$ values being set to zero). This procedure led to the positive values of $\Delta f''_p = 0.4(1)$ and $\Delta f''_s = 0.5(1)$ being in a good agreement with tabulated $\Delta f''_p = 0.43$ and $\Delta f''_s = 0.56$ for CuK_α radiation.[2]

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

Atomic coordinates are given in Table I, the molecular structure with bond lengths is shown in the Figure, bond angles are listed in Table II and torsion angles in Table III.

DISCUSSION

The 5-membered ring P(1)O(1)C(2)C(1)O(2) has an envelope conformation, the deviation of C(2) from the best P(1)O(1)C(1)O(2) plane being −0.504 Å. The dihedral angle between P(1)O(1)C(1)O(2) and C(1)C(2)O(1) planes is 34.6°. The second dioxaphospholane ring P(2)O(4)C(3)C(4)O(3) has a twist conformation.

Both P atoms have a tetrahedral coordination with the average endocyclic OPO angle of 95.6(3)°. The bond lengths P(1)—S(1) of 1.921(5) Å and P(2)—S(2) of 1.906(6) Å in fact coincide with the standard value of 1.91 Å.[3]

TABLE I

Atomic coordinates ($\times 10^4$). Anisotropic temperature factors are given 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)	8352(1)	9617(3)	2057(5)	3.9(2)	4.0(2)	3.6(2)	−0.9(2)	−0.4(2)	0.1(2)
P(2)	6672(2)	5744(3)	1474(5)	5.1(2)	3.8(2)	5.1(2)	−0.8(2)	−0.2(2)	−0.2(2)
S(1)	8448(2)	11374(3)	1954(5)	6.0(2)	3.7(2)	4.8(2)	−0.8(2)	−0.3(2)	−0.3(2)
S(2)	6486(2)	5021(4)	−545(6)	9.4(3)	6.4(3)	6.3(3)	−1.7(2)	−2.2(2)	−1.7(2)
O(1)	7836(3)	9062(8)	1046(10)	3.9(4)	4.2(5)	3.2(5)	−0.6(3)	0.2(4)	0.3(4)
O(2)	8152(3)	9117(8)	3771(11)	4.2(4)	5.3(5)	3.5(5)	−1.1(4)	−0.1(3)	0.9(4)
O(3)	6216(3)	6666(8)	2200(12)	3.4(4)	3.4(5)	6.5(6)	−0.6(3)	0.3(4)	0.9(5)
O(4)	7164(3)	6743(8)	1430(11)	3.9(4)	3.7(4)	3.7(5)	−0.4(4)	0.0(4)	−0.5(4)
N(1)	8891(4)	8826(11)	1518(16)	4.8(5)	3.7(6)	5.2(7)	1.1(5)	1.1(5)	1.1(6)
N(2)	6798(4)	4782(10)	2946(17)	6.0(6)	4.1(6)	5.0(7)	0.0(5)	−0.7(6)	−0.7(6)
N(3)	5959(5)	9892(11)	1774(15)	6.2(6)	4.3(6)	3.4(7)	1.0(5)	0.9(5)	1.8(6)
N(4)	5131(5)	8904(16)	−214(16)	3.4(6)	9(1)	7.2(9)	0.5(7)	−3.4(6)	0.4(9)
C(1)	7619(5)	8479(12)	3684(18)	5.3(7)	3.8(7)	3.4(7)	−0.3(6)	0.3(6)	0.0(7)
C(2)	7371(4)	8893(12)	2095(17)	2.0(5)	4.4(7)	3.6(7)	0.8(5)	−0.4(5)	0.5(6)
C(3)	6847(4)	7988(12)	1329(17)	1.9(5)	4.4(7)	4.7(8)	0.0(5)	−0.5(5)	0.0(7)
C(4)	6377(5)	7926(12)	2230(17)	3.9(6)	3.2(6)	4.8(8)	−0.7(5)	0.0(6)	−0.2(6)
C(5)	5937(6)	8707(15)	1456(19)	5.1(7)	4.2(7)	3.7(8)	0.0(7)	0.0(7)	1.4(7)
C(6)	5526(5)	8179(16)	380(22)	1.8(6)	8(1)	7(1)	−0.3(7)	−1.8(7)	0.4(9)
C(7)	9404(5)	9331(15)	807(20)	3.1(6)	5.8(9)	7(1)	0.6(7)	0.4(6)	−0.3(9)
C(8)	8882(6)	7512(14)	1726(24)	4.6(7)	5.2(9)	10(1)	2.3(6)	0.0(9)	0.0(9)
C(9)	6871(7)	5250(15)	4554(21)	8.7(9)	6(1)	4.2(9)	0.0(8)	0.5(8)	0.6(8)
C(10)	7021(8)	3540(14)	2684(23)	11(1)	4.1(8)	7(1)	2.1(8)	1(1)	1.3(8)
C(11)	5576(7)	10638(16)	1039(19)	6.1(9)	4.7(9)	4.4(9)	−1.3(8)	0.7(7)	0.2(8)
C(12)	5158(7)	10128(17)	69(22)	4.1(8)	5.0(9)	6(1)	−0.2(8)	0.5(8)	1.0(9)
C(13)	4752(6)	10963(23)	−620(22)	2.7(6)	12(2)	7(1)	2.9(9)	−1.6(7)	2(1)
C(14)	4775(9)	12170(21)	−324(31)	8(1)	7(1)	11(2)	3(1)	2(1)	3(1)
C(15)	5186(9)	12685(18)	657(27)	8(1)	6(1)	9(1)	0(1)	−1(1)	2(1)
C(16)	5588(6)	11894(17)	1331(27)	5.0(8)	5.0(9)	12(2)	1.8(7)	0.8(7)	2(1)

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

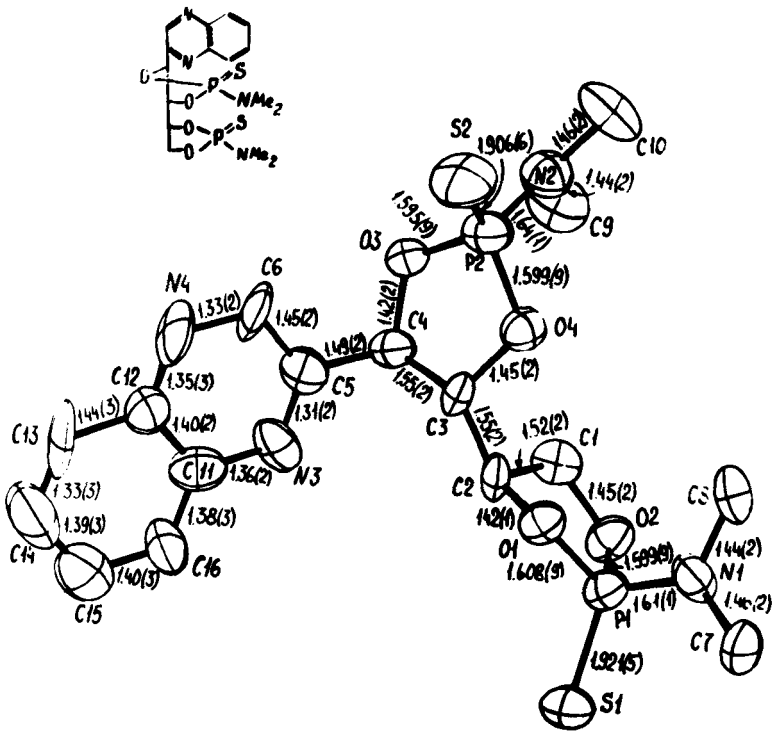


FIGURE 1 Structural parameters of **1**.

TABLE II

Bond angles ω (°).

Angle	ω	Angle	ω	Angle	ω
S(1)P(1)O(1)	116.0(4)	P(1)N(1)C(7)	125.5(9)	O(3)C(4)C(5)	110(1)
S(1)P(1)O(2)	114.3(4)	P(1)N(1)C(8)	119(1)	C(3)C(4)C(5)	112(1)
S(1)P(1)N(1)	114.9(5)	C(7)N(1)C(8)	116(1)	N(3)C(5)C(4)	116(1)
O(1)P(1)O(2)	96.4(5)	P(2)N(2)C(9)	119(1)	N(3)C(5)C(6)	123(1)
O(1)P(1)N(1)	105.5(6)	P(2)N(2)C(10)	123(1)	C(4)C(5)C(6)	121(1)
O(2)P(1)N(1)	107.9(6)	C(9)N(2)C(10)	115(1)	N(4)C(6)C(5)	118(1)
S(2)P(2)O(3)	115.7(4)	C(5)N(3)C(11)	118(1)	N(3)C(11)C(12)	120(1)
S(2)P(2)O(4)	115.4(4)	C(6)N(4)C(12)	119(2)	N(3)C(11)C(16)	119(2)
S(2)P(2)N(2)	116.1(5)	O(2)C(1)C(2)	104(1)	C(12)C(11)C(16)	120(2)
O(3)P(2)O(4)	94.8(5)	O(1)C(2)C(1)	106(1)	N(4)C(12)C(11)	122(2)
O(3)P(2)N(2)	104.0(6)	O(1)C(2)C(3)	109.7(9)	N(4)C(12)C(13)	121(2)
O(4)P(2)N(2)	108.3(6)	C(1)C(2)C(3)	115(1)	C(11)C(12)C(13)	117(2)
P(1)O(1)C(2)	108.8(7)	O(4)C(3)C(2)	108.5(9)	C(12)C(13)C(14)	121(2)
P(1)O(2)C(1)	112.3(8)	O(4)C(3)C(4)	104.2(9)	C(13)C(14)C(15)	122(2)
P(2)O(3)C(4)	115.3(8)	C(2)C(3)C(4)	114(1)	C(14)C(15)C(16)	118(2)
P(2)O(4)C(3)	111.7(7)	O(3)C(4)C(3)	106(1)	C(11)C(16)C(15)	121(2)

TABLE III

Torsion angles τ (°).

Angle	τ	Angle	τ
P(1)—O(1)—C(2)—C(1)	−37(1)	C(3)—C(4)—O(3)—P(2)	6.1(9)
O(1)—C(2)—C(1)—O(2)	33(1)	C(4)—O(3)—P(2)—O(4)	10(1)
C(2)—C(1)—O(2)—P(1)	−17.7(9)	O(3)—P(2)—O(4)—C(3)	−25(1)
C(1)—O(2)—P(1)—O(1)	−3(1)	C(1)—C(2)—C(3)—C(4)	71(2)
O(2)—P(1)—O(1)—C(2)	24(1)	C(2)—C(3)—C(4)—C(5)	98(2)
P(2)—O(4)—C(3)—C(4)	31(1)	C(3)—C(4)—C(5)—C(6)	98(2)
O(4)—C(3)—C(4)—O(3)	−22(1)		

The P—O bond lengths are in the range of 1.595–1.608 Å typical for analogous bonds in dioxaphospholane rings.[4] The P—N bond lengths (av. 1.625(6) Å) are in accordance with the value 1.62–1.64 Å found in other phosphorylated carbohydrates.[5,6]

The N-atoms have a planar coordination (sums of bond angles are 359.5 and 357° for N(1) and N(2), respectively).

The quinoxaline ring together with the C(4) atom is planar and, contrary to earlier suggestions, the orientation of this ring relative to the C(4)—C(5) bond corresponds to a closer approach of N(3) and C(3) but not O(3).

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