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SYNTHESIS OF *O*-METHYL *S*-(3,4,6-TRI-*O*-ACETYL-2-DEOXY-α-D-*arabino*-HEXOPYRANOSYL) (*R*)-DITHIOPHOSPHATE ION AND THE X-RAY CRYSTAL STRUCTURE OF THE DIPROPYLAMMONIUM SALT

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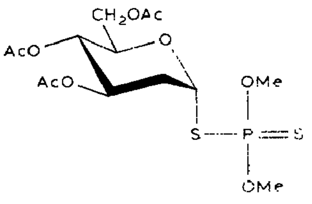
ABSTRACT

Elimination of one methyl group transformed *O,O'*-dimethyl *S*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl) dithiophosphate into the title ion with a chiral centre at phosphorus. The crystals of $C_{19}H_{36}NO_9PS_2$ (M_r 517.65) are monoclinic , space group $P2_1$, and have a = 16.721(9), b = 9.023(4), c = 19.797(8) Å, β = 109.95(4)°, V = 2807.6 Å^3, D_m = 1.21 and D_c = 1.22 g.cm^{-3} for Z = 4. The crystal structure has been determined by direct methods and refined to R = 0.052 for 4074 independent reflections. Both symmetry-independent pyranose rings have the $^4C_1$ conformation. The average C-1–S-1 and S-1–P bond lengths are 1.845(8) and 2.110(2) Å, respectively. The S-2–P–S-1–C-1 and O-1–P–O-2–C-13 torsion angles are in the range 170.9(6)–179.9(9)°. The nitrogen atoms of the dipropylammonium ions are involved in hydrogen bonds with the non-esterified oxygen atoms of the aglycon groups.

INTRODUCTION

Some *S*-glycosides and their derivatives are inhibitors of enzymes[1], and others provide intermediates with a protected anomeric center[2]. They have been used also in syntheses of thio analogs of some clinically important antibiotics[3], detergents[4], and glycosides.

O,O'-Dimethyl *S*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl) dithiophosphate (**1**), obtained from D-glucal[5], appeared to be a useful substrate for the synthesis of 2-deoxyglycosides[5] *via* the ready nucleophilic displacement of the *O,O'*-dimethyldithiophosphate group. The high yields (>90%) and the relatively mild conditions of these reactions suggested that 2-deoxy-*N*-glycosyl derivatives might be obtained by nucleophilic attack on nitrogen. However, the reaction that occurred was demethylation of the aglycon group of **1** (→**2**), which generated a new chiral centre at the phosphorus atom, and the title compound was the sole



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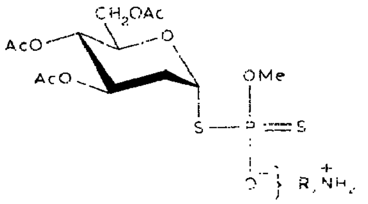

2a R = Pr

2b R = ^{i}Pr

diastereoisomeric product. The absolute configuration of the new chiral centre in the dipropylammonium salt **2a** has now been determined by the X-ray method.

EXPERIMENTAL

General methods. — Melting points were determined on a capillary melting apparatus and are uncorrected. Optical rotations were determined with a Hilger–Watts polarimeter. Microanalyses were carried out in the laboratory of Gdańsk University. ^{1}H-N.m.r. spectra were recorded with a Tesla BS-487 (80 MHz) instrument operating in the c.w. mode. T.l.c. was performed on Kieselgel 60 (Merck), and preparative t.l.c. was carried out on Silica Gel LSL$_{254}$ 5/40 (Merck). Mass spectra were obtained on a Varian MAT 711 instrument.

X-Ray structure determination. — The space group was determined from oscillation and Weissenberg photographs. All measurements for a crystal 0.55 × 0.55 × 0.18 mm were made on a Syntex P2$_1$ diffractometer equipped with a scintillation counter and graphite monochromator using MoKα radiation (λ = 0.71069 Å). The cell parameters were determined from a least-squares refinement of the setting angles of 15 reflections. Intensities of 8415 independent reflections were measured in the 2θ range 4–60° with the variable θ–2θ scan technique. The scan rate varied from 2.0 to 29.3°/min, depending on the intensity. Two reflections, which were monitored periodically, exhibited no significant variations in intensity during the period of data collection and 4074 reflections with $I > 3\sigma(I)$ were used in the analysis. The intensities were corrected for Lorentz and polarization factors, but not for absorption [μ(MoKα) = 2.9 cm^{-1}]. The structure was solved by direct methods using the MULTAN[6] suite of programs. A Fourier synthesis, based on the phases produced for the set with the highest combined figure of merit, showed the positions of P and S atoms. All C, N, and O atoms were localised on successive calculated Fourier and difference Fourier syntheses. Half of the positions of the hydrogen atoms were calculated based on the geometry of the molecule (C–H and N–H = 0.95 Å); the remaining hydrogen atoms were found from difference Fourier syntheses. The refinement of all non-H atoms with anisotropic temperature factors yielded a final R-index ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.052 and R_w-index [$= \Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ of 0.045. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F_o)$, where $\sigma(F_o)$ was taken from the counting statistic. During the last cycle of refinement, no parameter shifted more than one-fourth of its standard deviation. A final difference Fourier synthesis showed maximum and minimum electron densities of 0.23 and -0.21 e.Å^{-3}, respectively. All calculations were performed with the Syntex XTL/XTLE Structure Determination System[7]. Neutral-atom scattering factors were those listed in the International Tables for X-Ray Crystallography[8]. The anomalous dispersion was included for N, O, S, and P atoms.

Compound **1** was prepared as previously reported[5].

*Dipropylammonium O-methyl S-(3,4,6-tri-O-acetyl-2-deoxy-α-*D-arabino-*hexopyranosyl) (R)-dithiophosphate* (**2a**). — A mixture of **1** (0.43 g, 1 mmol), dipropylamine (3 mL, 22 mmol), and acetonitrile (3 mL) was stirred for 3 h. T.l.c. (carbon tetrachloride–acetone, 3:1) then showed that **1** (R_F 0.6) had vanished and that there was a single product (**2a**, R_F 0.12). The solvent and the excess of dipropylamine were evaporated under reduced pressure, and anhydrous methanol (15 mL) was evaporated 3 times from the residue (0.5 g, 94%) which was then recrystallised from anhydrous ether to give **2a**, m.p. 121–122°, $[\alpha]^{20}_{546}$ +153° (*c* 1, chloroform), $[M]^{20}_{546}$ +791°, R_F 0.72 (chloroform–methanol–ether, 3:2:2). ^{1}H-N.m.r. data ($CDCl_3$): δ 0.85 (t, 6 H, 2 Me), 1.20–1.75 (m, 4 H, 2 CH_3CH_2), 1.81–2.0 (d, 9 H, 3 OAc), 2.05–2.50 (m, 2 H, H-2,2), 2.64–2.90 (m, 4 H, 2 $CH_3CH_2CH_2$), 3.38 and 3.57 (2 d, 6 H, 2 Me), 3.75–4.20 (m, 3 H, H-5,6,6), 4.75–5.20 (m, 2 H, H-3,4), 5.75 (m, 1 H, H-1).

Anal. Calc. for $C_{19}H_{36}NO_9PS_2$: C, 44.10; H, 6.96; N, 2.70; S, 12.38. Found: C, 43.88; H, 6.91; N, 2.76; S, 11.94.

*Di-isopropylammonium O-methyl S-(3,4,6-tri-O-acetyl-2-deoxy-α-*D-arabino-*hexopyranosyl) dithiophosphate* (**2b**). — Replacement of dipropylamine with di-isopropylamine in the above reaction and preparative t.l.c. (twice in chloroform–acetone, 3:1) gave **2b** (0.45 g, 85%), m.p. 133–134° (from ether), $[\alpha]^{20}_{589}$ +64° (*c* 1, chloroform), $[M]^{20}_{589}$ +330°, $[\alpha]^{20}_{546}$ +96° (*c* 1, chloroform), $[M]^{20}_{546}$ +496°, R_F 0.73 (chloroform–methanol–ether, 3:2:2). ^{1}H-N.m.r. data ($CDCl_3$): δ 1.40 (d, 6 H, 2 Me), 2.02 (s, 9 H, 3 OAc), 2.13 and 2.32 (2 s, 2 H, H-2,2), 3.25–3.75 (m, 1 H, Me_2CH), 3.56 and 3.76 (2 d, 6 H, 2 Me), 4.05–4.30 (m, 3 H, H-5,6,6), 4.80–5.35 (m, 2 H, H-3,4), 5.95 (m, 1 H, H-1), 7.80 (N-H).

Anal. Calc. for $C_{19}H_{36}NO_9PS_2$: C, 44.10; H, 6.96; N, 2.70. Found: C, 43.90; H, 7.04; N, 3.03.

RESULTS AND DISCUSSION

The crystals of **2a** are built from the symmetry-independent molecules (A and B). The numbering scheme and the overall conformation of these molecules and the molecular packing diagram are shown in Figs. 1 and 2. Tables I–V list the atomic positional and thermal parameters, bond distances and angles, selected torsion angles, and hydrogen-bond distances and angles.

Both molecules have almost the same geometry. The average C–C and C–O bond lengths for pyranose rings are 1.520(19) and 1.411(9) Å, respectively. The

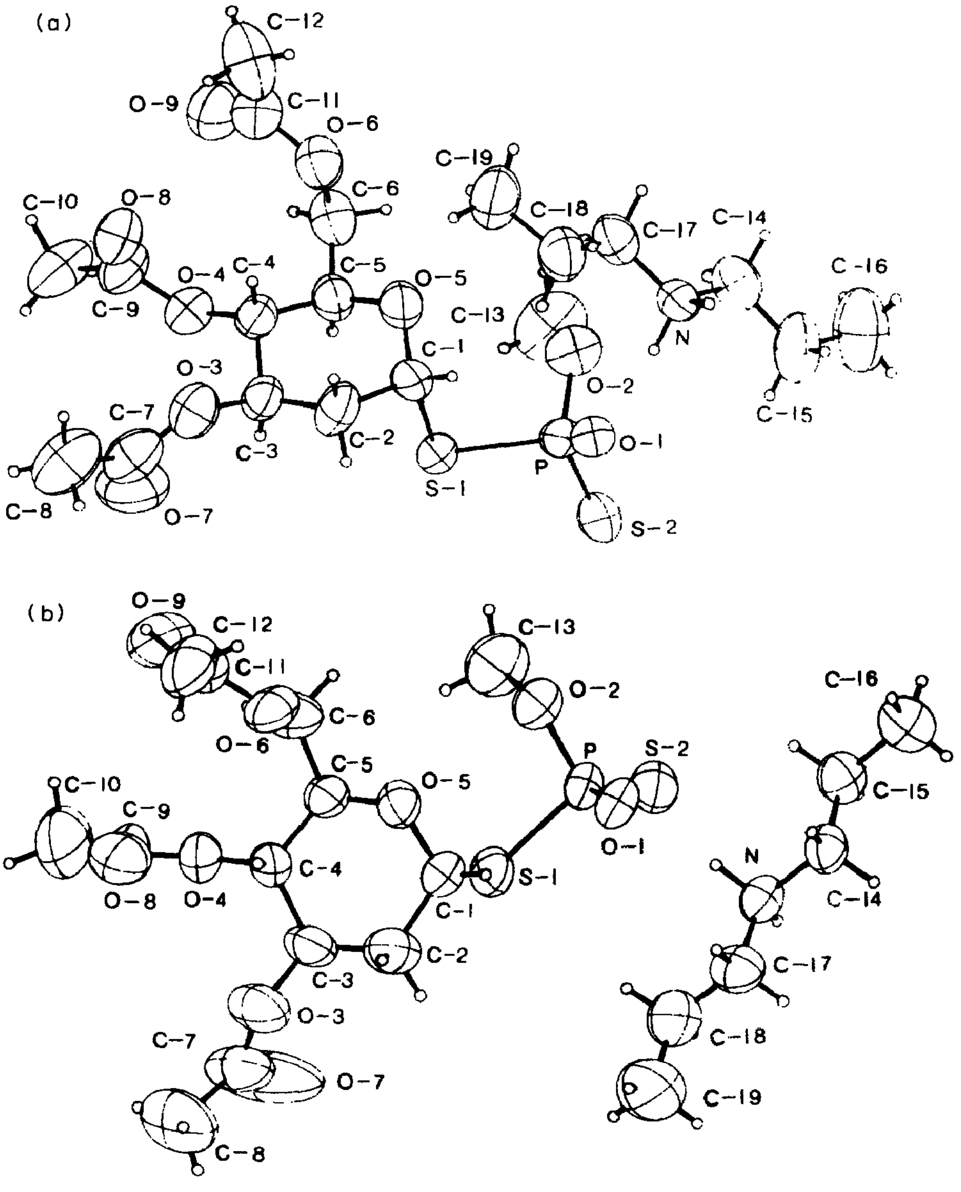

Fig. 1. ORTEP drawings showing atom numbering in molecules A (a) and B (b). The non-hydrogen atoms are represented by 50% probability ellipsoids and the hydrogen atoms are drawn as spheres of arbitrary size.

C-5–O-5 bond lengths are slightly longer than the C-1–O-5 bonds. These differences accord with the theoretical predictions for α-D-pyranosides[9]. The C-1–S-1 bond lengths fall in the range observed in thiocarbohydrates[10]. Bond angles at O-5 are similar to those for other pyranosides[9]. Most of the endocyclic angles are close to tetrahedral except that of C-2–C-1–O-5 with an average value of 112.3(3)°

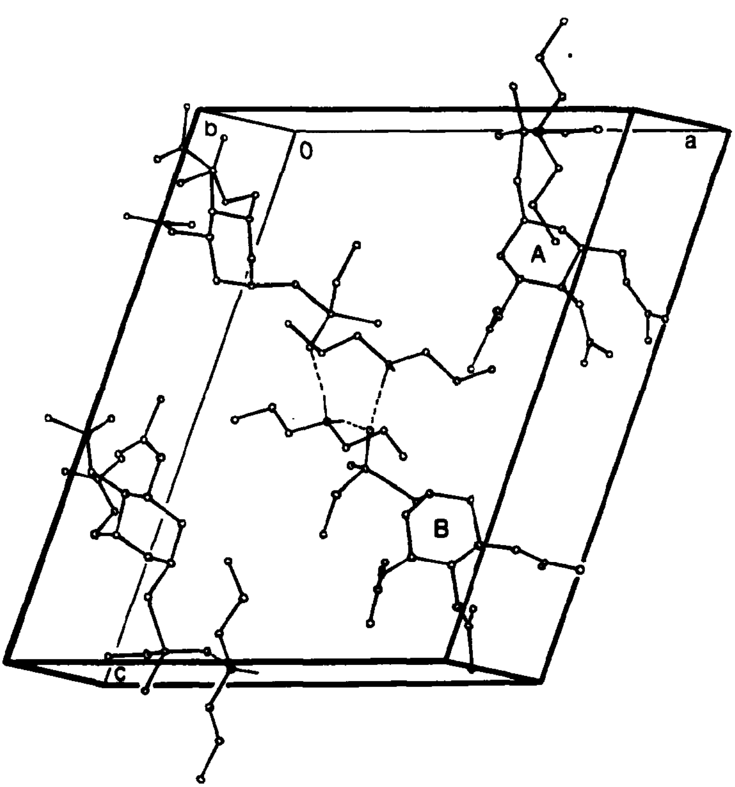

Fig. 2. Molecular packing in the crystal of dipropylammonium *O*-methyl *S*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl) (*R*)-dithiophosphate (**2a**). The hydrogen atoms have been removed for clarity except those involved in hydrogen bonds.

and C-1–C-2–C-3 in molecule B with a value of 112.1(6)°. Characteristic for the "anomeric" center, the O-5–C-1–S-1 valency angles of 113.4(4) and 113.9(5)° are closer to the value of the S–C–S angle in 1,5-dithio-α-D-pyranosides[11] rather than to the average 111.9° in analogous *S*-glycosides[12].

The pyranose rings exhibit some flattening at C-2. The ring puckering parameters[13,14] are Q = 0.538(6) Å, θ = 5.6(7)°, φ = 280(7)° for molecule A, and are 0.547(7) Å, 7.6(7)°, and 293(5)° for molecule B. The distortion of these rings from the $^4C_1$ chair conformation toward the S_5 and/or $B_{2,5}$ geometry is similar (in the 3σ range) and small.

The geometry of external C–O bonds (including the C-6–O-6 bonds) and of planar acetoxy groups is normal and similar to other acetylated (in positions 3*e*, 4*e*, and 6) carbohydrates with the $^4C_1$ conformation. According to the terminology proposed by Sundaralingam[15], the acetoxymethyl groups in both carbohydrate moieties have the energetically preferred *gauche–gauche* conformations[16] with torsion angles around the C-6–O-6 bond of −124(1) and −143(1)° for molecules A and B, respectively.

TABLE I

FRACTIONAL ATOMIC COORDINATES, EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR NON H ATOMS, AND COVALENT BOND LENGTHS FOR H ATOMS[a]

Atom	*Molecule A*				*Molecule B*			
	x	y	z	B_{eq} (Å)^2 or *X–H* (Å)	x	y	z	B_{eq} (Å)^2 or *X–H* (Å)
P	6438(1)	5000(fixed)	208(1)	4.2(1)	5397(1)	4724(2)	6296(1)	4.1(1)
S-1	6996(1)	6193(2)	1170(8)	4.9(1)	6637(1)	3933(2)	6851(1)	5.1(1)
S-2	6232(1)	6488(2)	−540(1)	6.6(2)	4649(1)	3029(2)	6173(1)	6.0(2)
O-1	5704(2)	4116(4)	259(2)	4.4(3)	5409(2)	5566(4)	5655(2)	4.7(3)
O-2	7120(2)	3775(5)	207(2)	5.8(4)	5233(2)	5964(5)	6801(2)	5.4(4)
O-3	7713(3)	6466(6)	3646(2)	6.2(4)	9586(3)	5105(6)	7767(3)	8.8(6)
O-4	9319(2)	5999(5)	3410(2)	5.4(4)	8920(3)	6087(6)	8850(2)	7.2(5)
O-5	7841(3)	3845(5)	1974(2)	5.4(4)	7163(2)	6774(4)	7200(2)	4.8(3)
O-6	9340(3)	2448(5)	2865(2)	6.2(4)	7638(3)	9122(5)	8160(2)	6.4(4)
O-7	8177(4)	8772(7)	3625(3)	10.9(7)	9746(5)	2778(8)	7989(6)	20.1(14)
O-8	9589(3)	4733(7)	4428(2)	8.4(5)	9788(3)	8046(8)	8971(3)	9.9(6)
O-9	10664(3)	2929(7)	3555(3)	8.2(5)	7986(4)	9931(7)	9284(3)	9.6(6)
N	5775(3)	990(5)	63(2)	4.6(4)	4873(3)	3709(5)	4389(2)	4.6(4)
C-1	7091(4)	4680(8)	1826(3)	5.2(6)	7240(4)	5587(8)	6773(3)	5.6(6)
C-2	6993(4)	5367(9)	2514(3)	6.0(7)	8174(4)	5212(9)	6892(4)	7.0(7)
C-3	7793(3)	6147(8)	2955(3)	4.7(5)	8698(4)	5070(8)	7681(4)	6.5(7)
C-4	8568(3)	5177(7)	3063(3)	4.4(5)	8517(4)	6386(8)	8099(3)	5.5(6)
C-5	8595(4)	4637(8)	2348(3)	5.0(5)	7583(4)	6541(7)	7941(7)	4.9(5)
C-6	9323(4)	3648(8)	2409(3)	6.3(7)	7339(4)	7763(8)	8337(4)	6.7(7)
C-7	7917(5)	7811(10)	3920(4)	7.7(8)	10048(5)	3870(10)	7963(5)	10.2(10)
C-8	7819(5)	7948(12)	4646(4)	9.5(10)	10962(6)	4152(12)	8112(7)	13.2(14)
C-9	9785(4)	5655(8)	4098(3)	5.9(6)	9546(5)	7042(12)	9212(12)	8.4(9)
C-10	10555(5)	6643(11)	4357(4)	8.4(9)	9862(7)	6604(15)	9985(7)	12.8(14)
C-11	10046(4)	2209(8)	3434(3)	6.1(6)	7927(4)	10132(8)	8680(4)	6.4(7)
C-12	9947(6)	956(12)	3857(5)	10.5(10)	8222(6)	11548(10)	8400(4)	8.5(9)
C-13	7921(5)	4155(12)	163(4)	9.8(10)	5150(5)	5577(11)	7485(4)	9.0(9)
C-14	6037(4)	789(8)	−587(4)	6.5(7)	4084(4)	4389(7)	3891(3)	4.9(6)
C-15	5370(4)	1404(11)	1249(4)	8.2(9)	3377(4)	4267(8)	4193(4)	5.7(6)
C-16	5574(6)	1112(14)	−1920(5)	11.5(12)	2567(4)	5022(10)	3697(4)	7.4(8)
C-17	6456(4)	474(8)	731(4)	5.9(6)	5639(4)	3833(8)	4169(4)	6.2(6)
C-18	6168(4)	582(9)	1373(4)	6.8(7)	6391(5)	3081(10)	4670(4)	7.9(8)
C-19	6887(5)	213(11)	2050(4)	8.1(9)	7140(6)	3097(17)	4463(7)	14.7(16)
H C-1	663	403	165	0.93	699	594	629	0.95

TABLE I *(continued)*

Atom	*Molecule A*				*Molecule B*			
	x	y	z	B_{eq} *(Å)*^{2} *or X–H (Å)*	x	y	z	B_{eq} *(Å)*^{2} *or X–H (Å)*
H-1–C-2	687	456	278	0.96	842	597	670	0.95
H-2–C-2	652	602	237	0.95	821	429	667	0.95
H–C-3	786	706	273	0.86	857	417	788	0.96
H–C-4	852	434	333	0.94	873	727	796	0.95
H–C-5	868	548	212	0.92	742	565	812	0.95
H-1–C-6	923	327	194	0.95	674	782	820	0.95
H-2–C-6	986	419	258	0.98	758	761	884	0.95
H-1–C-8	790	703	488	0.94	1117	433	850	0.75
H-2–C-8	724	827	457	0.97	1109	490	782	0.96
H-3–C-8	819	867	495	0.96	1109	323	795	0.95
H-1–C-10	1072	683	393	0.99	955	735	1018	1.01
H-2–C-10	1103	610	468	0.96	1046	684	1027	0.99
H-3–C-10	1045	750	454	0.90	973	568	1015	0.94
H-1–C-12	961	38	365	0.77	866	1127	830	0.86
H-2–C-12	981	131	425	0.94	834	1231	876	0.96
H-3–C-12	1049	46	403	0.97	776	1190	798	0.97
H-1–C-13	813	496	46	0.92	483	468	751	0.98
H-2–C-13	787	428	−31	0.91	488	641	762	0.96
H-3–C-13	826	329	36	0.97	571	550	782	0.95
H-1–N	527	45	−1	0.94	478	264	445	0.99
H-2–N	567	202	10	0.95	501	427	482	0.95
H-1–C-14	611	−26	−66	0.97	394	385	345	0.95
H-2–C-14	656	126	−52	0.95	420	538	382	0.94
H-1–C-15	529	242	−119	0.94	354	479	464	0.96
H-2–C-15	487	87	−130	0.94	325	329	425	0.93
H-1–C-16	538	16	−202	0.92	248	460	329	0.87
H-2–C-16	617	108	−188	0.98	262	608	365	0.96
H-3–C-16	528	170	−233	0.96	208	486	385	0.97
H-1–C-17	695	108	81	0.96	578	485	416	0.95
H-2–C-17	660	−52	67	0.95	551	341	371	0.94
H-1–C-18	573	−12	133	0.95	624	208	472	0.95
H-2–C-18	597	155	141	0.94	656	357	512	0.94
H-1–C-19	742	70	208	0.99	700	253	403	0.96
H-2–C-19	698	−80	210	0.93	754	249	483	0.97
H-3–C-19	675	59	246	0.98	740	392	442	0.88

[a] Values of positional parameters are $\times 10^4$ for non-H atoms and $\times 10^3$ for the H atoms, and $B_{eq} = {}^1/_3\Sigma B_{ii}$, $B_{iso} = 10$ Å^2 for all H atoms. The *y* coordinate of P from molecule A was not refined.

TABLE II

BOND LENGTHS (Å)[a]

	Molecule			Molecule	
	A	*B*		*A*	*B*
P–S-1	2.108(2)	2.112(2)	O-9–C-11	1.174(9)	1.180(9)
P–S-2	1.941(2)	1.938(3)	N–C-14	1.505(8)	1.484(8)
P–O-1	1.495(4)	1.484(4)	N–C-17	1.495(8)	1.491(9)
P–O-2	1.589(5)	1.586(4)	C-1–C-2	1.555(9)	1.536(10)
S-1–C-1	1.853(7)	1.837(7)	C-2–C-3	1.555(9)	1.513(10)
O-2–C-13	1.413(10)	1.451(9)	C-3–C-4	1.517(9)	1.535(10)
O-3–C-3	1.448(7)	1.436(8)	C-4–C-5	1.513(8)	1.493(9)
O-3–C-7	1.326(10)	1.335(11)	C-5–C-6	1.481(10)	1.480(10)
O-4–C-4	1.417(7)	1.432(8)	C-7–C-8	1.506(11)	1.477(14)
O-4–C-9	1.355(7)	1.360(10)	C-9–C-10	1.505(11)	1.480(14)
O-5–C-1	1.407(8)	1.397(8)	C-11–C-12	1.449(12)	1.538(11)
O-5–C-5	1.417(8)	1.421(7)	C-14–C-15	1.507(10)	1.500(9)
O-6–C-6	1.404(8)	1.413(9)	C-15–C-16	1.504(12)	1.534(10)
O-6–C-11	1.342(8)	1.336(8)	C-17–C-18	1.509(10)	1.475(11)
O-7–C-7	1.207(11)	1.115(12)	C-18–C-19	1.502(10)	1.445(14)
O-8–C-9	1.172(9)	1.167(12)			

[a]Estimated standard deviations in parentheses.

TABLE III

VALENCY ANGLES (DEGREES)[a]

	Molecule			Molecule	
	A	*B*		*A*	*B*
S-1–P–S-2	104.2(1)	106.0(1)	O-4–C-4–C-3	109.8(5)	107.7(5)
S-1–P–O-1	109.4(2)	108.7(2)	O-4–C-4–C-5	108.5(5)	108.4(5)
S-1–P–O-2	105.1(2)	105.1(2)	C-3–C-4–C-5	110.5(5)	110.5(5)
S-2–P–O-1	119.0(2)	119.6(2)	O-5–C-5–C-4	110.2(5)	109.5(5)
S-2–P–O-2	114.8(2)	113.1(2)	O-5–C-5–C-6	107.4(5)	107.8(5)
P–S-1–C-1	99.4(2)	98.7(2)	C-4–C-5–C-6	113.9(5)	114.9(6)
P–O-2–C-13	121.8(5)	120.8(4)	O-3–C-7–O-7	123.0(8)	121.6(9)
C-3–O-3–C-7	118.3(5)	119.3(6)	O-3–C-7–C-8	111.7(7)	111.8(8)
C-4–O-4–C-9	118.6(5)	116.2(6)	O-7–C-7–C-8	125.3(8)	126.6(10)
C-1–O-5–C-5	114.2(5)	113.7(5)	O-4–C-9–O-8	123.3(7)	125.4(8)
C-6–O-6–C-11	118.9(5)	117.8(5)	O-4–C-9–C-10	109.8(6)	108.8(8)
C-14–N–C-17	111.2(5)	115.6(5)	O-8–C-9–C-10	127.0(7)	125.8(9)
S-1–C-1–O-5	113.4(4)	113.9(5)	O-6–C-11–O-19	122.8(7)	124.0(7)
S-1–C-1–C-2	108.1(4)	111.6(5)	O-6–C-11–C-12	111.7(7)	111.4(6)
O-5–C-1–C-2	112.6(5)	112.0(6)	O-9–C-11–C-12	125.4(7)	124.4(7)
C-1–C-2–C-3	111.0(5)	112.1(6)	N–C-14–C-15	110.7(6)	110.3(5)
O-3–C-3–C-2	106.9(5)	109.4(6)	C-14–C-15–C-16	112.3(7)	110.9(6)
O-3–C-3–C-4	109.4(5)	107.8(6)	N–C-17–C-18	111.1(6)	112.9(6)
C-2–C-3–C-4	111.1(5)	109.9(6)	C-17–C-18–C-19	110.4(6)	115.3(8)

[a]Estimated standard deviations in parentheses.

TABLE IV

SELECTED TORSION ANGLES (DEGREES)[a]

	Molecule	
	A	*B*
C-1–C-2–C-3–C-4	−48.7(10)	−47.1(11)
C-2–C-3–C-4–C-5	53.7(10)	53.0(11)
C-3–C-4–C-5–O-5	−57.8(12)	−59.7(12)
C-4–C-5–O-5–C-1	59.9(10)	63.1(10)
C-5–O-5–C-1–C-2	−55.7(10)	−57.4(10)
O-5–C-1–C-2–C-3	49.3(11)	49.3(12)
C-4–C-5–C-6–O-6	54.6(12)	58.7(11)
O-5–C-5–C-6–O-6	−67.7(10)	−63.7(11)
S-2–P–S-1–C-1	176.6(5)	170.9(6)
O-2–P–S-1–C-1	−62.3(6)	−69.1(6)
O-1–P–O-2–C-13	179.9(9)	178.1(6)
P–S-1–C-1–O-5	86.1(6)	71.8(6)
S-1–C-1–O-5–C-5	67.5(10)	70.4(10)

[a]Estimated standard deviations in parentheses.

TABLE V

HYDROGEN-BOND DISTANCES (Å) AND ANGLES (DEGREES)[a]

D–H···A (code)	*D···A*	*H···A*	*D–H–A*
Molecule A			
N–H-1···O-1 $(1-x, -\tfrac{1}{2}+y, -z)$	2.881(6)	1.95	170
N–H-2···O-1 (x, y, z)	2.855(6)	1.92	169
Molecule B			
N–H-1···O-1 $(1-x, -\tfrac{1}{2}+y, -z)$	2.871(6)	1.90	168
N–H-2···O-1 (x, y, z)	2.892(6)	1.95	171

[a]Estimated standard deviations in parentheses.

The absolute configuration of the chiral dithiophosphate moiety in **2a** was determined as *R* with reference to the carbohydrate moiety. In both symmetry-independent ions, the phosphorus atoms have almost identical tetrahedral arrangements but differently distorted compared to those observed in *O,O'*-diesterified phosphorodithioates[17–25]. The average P–S bond lengths are 2.110(2) Å for the P–S-1 bond and 1.940(2) Å for the P–S-2 bond. According to Pauling's convention for summing covalent radii[26], the lengths of P–S single and double bonds are 2.14 and 1.94 Å, respectively. By comparison, our observed bond lengths (not corrected for thermal motion) indicate single-bond character in the first and some double-bond character in the second case. The average P–O-1 and P–O-2 bond lengths of 1.490(6) and 1.588(2) Å, respectively, are characteristic for deprotonated and esterified oxygen atoms in the majority of other compounds containing P–O bonds. The largest value of the valency angle around the phosphorus atom exists between non-esterified S-2 and O-1. The average value of the S-2–P–O-1 angle is 119.3(3)°. Similar values are characteristic for non-esterified S–P–S angles in phosphorodithioate structures, whereas, in this compound, the average S-1–P–S-2 angle is 105.1(9)°. The average value of the O-1–P–O-2 angle of 103.6(1)° is larger by ~7° than in *O,O′*-diesterified phosphorodithioates. With respect to the O–P–O–C and S–P–S–C bond systems, the aglycon groups have the *ap,ap* conformation corresponding to the preferred *sc,sc* conformation among phosphate ester structures without obvious steric hindrances[27,28].

The relative orientation of the aglycon group and the carbohydrate moiety is described by the torsion angles around the glycosidic bond C-1–S-1 and the S-1–P bond. The O-5–C-1–S-1–P torsion angles are 86.1(7) and 71.8(7)° for molecules A and B, respectively. The differences between the torsion angles around the S-1–P bond in molecules A and B are ~7°. The value of the valency angles C-1–S-1–P are 99.4(2) and 98.7(2)°. For comparison, the C–S–C angles in other 1-thiopyranosides varied[29,30] in the range 98.0–103.3°.

Both symmetry-independent dipropylammonium cations have the chain conformation with average torsion angles of −175.5(9) and ±177.2(5)°. The nitrogen atoms and non-esterified O-1 atoms form infinite zigzag chains of the hydrogen bonds along the *b* axis. There were no significant intramolecular steric interactions, but some intermolecular contacts occur, corresponding to van der Waals forces. This is the main reason of differences between molecules A and B.

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REFERENCES

1 E. Zeffren and P. Hall, *The Study of Enzyme Mechanisms*, Wiley Interscience, New York, 1973, pp. 259–264.
2 P. Cuatrecasas, *Adv. Enzymol. Relat. Areas Mol. Biol.*, 36 (1972) 29–89.
3 G. Kavadias, R. Droghini, Y. Pepin, M. Menard, and P. Lapointe, *Can. J. Chem.*, 57 (1979) 1056–1063.
4 J. Cuomo, J. Merrifield, and Y. Keana, *J. Org. Chem.*, 45 (1980) 4216–4219.
5 J. Borowiecka and M. Michalska, *Carbohydr. Res.*, 68 (1979) C8–C10.
6 G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 27 (1971) 368–376.
7 *Syntex XTL/XTLE Structure Determination System*, Syntex Analytical Instruments, Cupertino, 1976.
8 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.
9 G. A. Jeffrey, J. A. Pople, J. S. Binkley, and S. Vishveshwara, *J. Am. Chem. Soc.*, 100 (1978) 373–379.
10 S. Takagi and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 34 (1978) 816–820.
11 R. L. Girling and G. A. Jeffrey, *Acta Crystallogr., Sect. B*, 30 (1974) 327–333.

12 S. Pérez and C. Vergelati, *Acta Crystallogr., Sect. B,* 40 (1984) 294–299.
13 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.
14 P. Luger and R. Bülow, *J. Appl. Crystallogr.*, 16 (1983) 431–432.
15 M. Sundaralingam, *Biopolymers,* 6 (1968) 189–213.
16 S. Pérez, J. St-Pierre, and R. H. Marchessault, *Can. J. Chem.*, 56 (1978) 2866–2871.
17 P. Coppens, C. H. MacGillavry, S. G. Hovenkamp, and H. Douwes, *Acta Crystallogr.*, 15 (1962) 765–769.
18 J. F. McConnell and V. Kastalsky, *Acta Crystallogr.*, 22 (1967) 853–859.
19 V. Kastalsky and J. F. McConnell, *Acta Crystallogr., Sect. B,* 25 (1969) 909–915.
20 T. Ito, T. Igarashi, and H. Hagihara, *Acta Crystallogr., Sect. B,* 25 (1969) 2303–2309.
21 S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 8 (1969) 2410–2421.
22 S. L. Lawton, *Inorg. Chem.*, 9 (1970) 2269–2274.
23 P. S. Shetty and Q. Fernando, *J. Am. Chem. Soc.*, 92 (1970) 3964–3969.
24 J. P. Hazel and R. L. Collin, *Acta Crystallogr., Sect. B,* 28 (1972) 2279–2287.
25 A. E. Kalinin, V. G. Andrianov, and Yu. T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1979) 783–786.
26 L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, 1960, pp. 221–228.
27 M. Sundaralingam, *Biopolymers,* 7 (1969) 821–860.
28 E. Shefter, M. Barlow, R. A. Sparks, and K. N. Trueblood, *Acta Crystallogr., Sect. B,* 25 (1969) 895–909.
29 D. C. Carter, J. R. Ruble, and G. A. Jeffrey, *Carbohydr. Res.*, 102 (1982) 59–67.
30 S. Nordenson and G. A. Jeffrey, *Acta Crystallogr., Sect. B,* 36 (1980) 1214–1216.