X-ray structure determination of the phosphite triester of methyl β-D-ribopyranoside; CNDO-2 calculation

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Abstract. The phosphite triester (**6**), the *O,O,O*-thiophosphate triester (**7**), and the phosphate triester (**8**) of methyl β-D-ribopyranoside were prepared. Crystal structures of **6** and **7** were determined by X-ray diffraction. Quantum-chemical calculations were performed on **6**. They clearly demonstrate that the positive charge on phosphorus is relatively high. This high charge is a result of the strain in the ester moiety of **6**.

Introduction

In a previous paper[1] CNDO-2 calculations were reported on a series of phosphites: $(MeO)_3P$ (**1**), $MeO\overline{POCH_2CH_2CH_2O}$ (**2**), $MeO\overline{POCH_2CH_2O}$ (**3**), $P(OCH_2)_3CH$ (**4**), and $OP(OCH_2)_2CH$ (**5**). It was found by these calculations and by protonation experiments that the phosphorus basicity of these compounds decreased in the order $1 > 2 > 3 > 4 > 5$; this sequence can be attributed to rehybridization of the ester oxygen atoms and to lone-pair orientations of these oxygen atoms relative to the phosphorus lone pair.

The geometry used for **5** was estimated from a larger bicyclic system. In order to obtain additional structural information on phosphite esters and moreover to determine the influence on the sugar ring, we have now determined the crystal structures of the phosphite triester **6** and the *O,O,O*-thiophosphate triester **7**. We used the geometries found by X-ray analysis as input for a CNDO-2 calculation.

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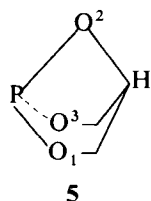
Determination of the crystal structures

*Phosphite triester of methyl β-D-ribopyranoside, **6***

Crystal data.—Crystals of **6** are monoclinic needles of space group $P2_1$ and with 6 molecules in a unit cell of dimensions $a = 1.33023(6)$, $b = 0.62021(3)$, $c = 1.48115(9)$ nm and $\beta = 94.201(5)°$. The needle axis is along 010. The crystal used for the intensity measurements was a needle of length 3 mm and cross section 0.12×0.22 mm, mounted in a thin-walled glass capillary. A number of 2048 reflexions with intensities above the 2σ-level was collected on a NONIUS CAD4 automatic single crystal diffractometer using graphite monochromatised $CuK\alpha$ radiation. No absorption correction was applied. Because of its length the crystal was not bathed in the incident beam and the intensities had to be corrected for the variation of the irradiated volume of the crystal. With the needle axis along the φ-axis of the diffractometer the correction factor is $[1-(k^2 b^{*2} \lambda^2)/4]^{\frac{1}{2}}$ and thus is a function of k only.

Structure determination and refinement. The structure was solved from an (E^2-1)-Patterson synthesis. Because of overlap of Harker and non-Harker P—P vectors the interpretation of the Patterson function was not straightforward.

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[1] *L. J. VandeGriend, J. G. Verkade, J. F. M. Pennings* and *H. M. Buck*, J. Am. Chem. Soc. **99**, 2459 (1977).

After locating 2 of the 3 P atoms in the asymmetric unit a Patterson minimum function based on the 4 P atoms in the unit cell thus obtained yielded the remaining non-hydrogen atoms except those of the OCH$_3$ groups. These were found from a subsequent difference Fourier synthesis. Refinement proceeded by means of anisotropic least squares calculations. The variation of the irradiated volume was taken into account by introducing a separate scale factor for each of the reciprocal lattice planes h0l, h1l, ... Since only part of the hydrogen atoms was indicated in a difference Fourier synthesis, in the final refinement cycles the hydrogen atoms were introduced at calculated positions but not refined.

The final R value was 8.1 %. The final coordinates are listed in Table I. The atomic numbering is indicated in Fig. 1. The bond lengths and interbond angles are collected in Tables II and III, respectively.

Thiophosphate O,O,O-triester of methyl β-D-ribopyranoside, 7

Crystal data.—Crystals of 7 are orthorhombic with space group P 2$_1$2$_1$2$_1$ and 4 molecules in a unit cell of dimensions a = 0.64379(3), b = 1.02856(4), c = 1.39070(5) nm. A number of 983 independent reflexions with intensities above the 2σ-level was collected on a NONIUS CAD4 automatic single crystal diffractometer using graphite monochromatised CuKα radiation. No absorption correction was applied.

Table I Compound 6. Fractional coordinates (× 10⁴). Estimated standard deviations in the last digit are given in parentheses.

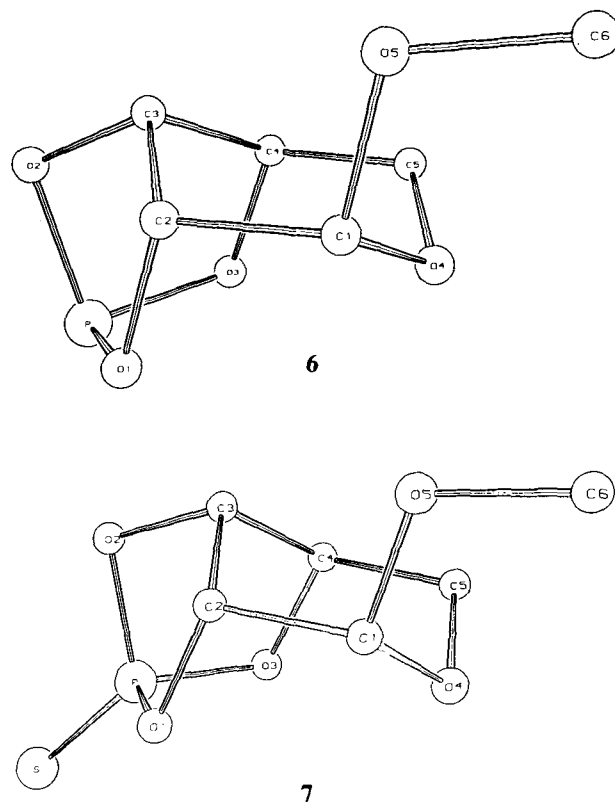|	x	y	z
P(1)	3607(3)	10091(9)	381(3)
O(11)	2711(6)	8826(16)	867(6)
O(21)	4369(6)	7966(19)	439(8)
O(31)	3213(8)	9713(18)	−686(7)
O(41)	1513(7)	6785(17)	−582(6)
O(51)	1874(7)	3474(18)	143(7)
C(11)	1810(8)	5805(23)	235(8)
C(21)	2763(9)	6509(22)	688(9)
C(31)	3637(9)	6400(25)	57(11)
C(41)	3267(10)	7345(27)	−855(9)
C(51)	2257(12)	6597(29)	−1234(9)
C(61)	979(12)	2494(33)	−243(13)
P(2)	2074(3)	5309(8)	3531(3)
O(12)	1339(7)	4049(16)	4196(6)
O(22)	2838(6)	3200(19)	3479(7)
O(32)	1480(7)	4848(18)	2549(6)
O(42)	−130(7)	1880(18)	2973(7)
O(52)	378(7)	−1313(19)	3711(7)
C(12)	324(8)	1041(24)	3778(9)
C(22)	1350(9)	1736(24)	4040(9)
C(32)	2060(9)	1605(25)	3246(11)
C(42)	1509(11)	2451(29)	2385(9)
C(52)	467(13)	1628(34)	2207(10)
C(62)	−595(13)	−2317(29)	3565(14)
P(3)	4871(3)	10000(0)	2794(3)
O(13)	5836(6)	8764(16)	2396(6)
O(23)	4125(7)	7819(19)	2677(7)
O(33)	5140(7)	9601(15)	3880(6)
O(43)	6906(7)	6787(16)	3928(6)
O(53)	6596(6)	3432(17)	3189(7)
C(13)	6720(8)	5787(23)	3098(8)
C(23)	5772(9)	6444(22)	2565(8)
C(33)	4835(8)	6292(25)	3094(10)
C(43)	5108(11)	7257(25)	4059(9)
C(53)	6089(11)	6556(26)	4504(9)
C(63)	7468(11)	2509(28)	3676(11)

6

7

Fig. 1. ORTEP drawing of molecules 6 and 7.

Table III Compound 6. Interbond angles in degrees. Estimated standard deviations in the last digit are given in parentheses.

	Molecule 1	Molecule 2	Molecule 3	Average
O(1)PO(2)	93.3(6)°	92.7(5)°	93.4(5)°	93.2(4)°
O(1)PO(3)	99.4(5)	100.5(5)	99.3(5)	99.7(4)
O(2)PO(3)	95.0(6)	94.5(6)	93.7(5)	94.4(4)
PO(1)C(2)	110.2(8)	111.2(8)	109.9(7)	110.4(5)
PO(2)C(3)	96.9(7)	96.9(7)	97.0(8)	96.9(5)
PO(3)C(4)	106.6(8)	107.5(8)	108.5(7)	107.5(6)
O(1)C(2)C(1)	109.1(10)	108.3(11)	107.5(10)	108.3(7)
O(1)C(2)C(3)	101.5(10)	100.6(11)	102.1(10)	101.5(7)
O(2)C(3)C(2)	104.2(12)	104.2(12)	105.9(11)	104.8(8)
O(2)C(3)C(4)	104.5(12)	104.8(12)	103.9(11)	104.4(8)
O(3)C(4)C(3)	104.3(11)	102.8(11)	102.7(10)	103.3(8)
O(3)C(4)C(5)	108.4(12)	109.5(13)	109.4(12)	109.1(9)
O(4)C(1)C(2)	117.0(11)	117.1(12)	115.9(11)	116.6(8)
C(1)C(2)C(3)	112.1(11)	113.0(11)	113.7(10)	112.9(7)
C(2)C(3)C(4)	108.1(10)	109.5(10)	107.6(10)	108.3(7)
C(3)C(4)C(5)	116.0(12)	114.7(13)	115.5(12)	115.4(9)
C(4)C(5)O(4)	111.6(11)	112.6(12)	112.7(11)	112.3(8)
C(5)O(4)C(1)	112.6(10)	113.8(11)	112.9(10)	113.1(7)
C(2)C(1)O(5)	106.6(10)	105.3(10)	102.8(9)	104.9(7)
O(4)C(1)O(5)	111.6(10)	109.5(11)	112.1(10)	111.1(7)
C(1)O(5)C(6)	114.2(11)	113.2(11)	110.4(10)	112.6(7)

Table II Compound 6. Bond lengths in Å. Estimated standard deviations in the last digit are given in parentheses.

	Molecule 1	Molecule 2	Molecule 3	Average
P−O(1)	1.637(10)	1.636(11)	1.641(10)	1.639(7)
P−O(2)	1.661(12)	1.662(12)	1.679(11)	1.668(7)
P−O(3)	1.645(11)	1.629(10)	1.641(10)	1.638(7)
O(1)−C(2)	1.464(17)	1.453(18)	1.464(17)	1.460(10)
O(2)−C(3)	1.460(17)	1.455(17)	1.444(17)	1.453(10)
O(3)−C(4)	1.492(20)	1.507(21)	1.479(18)	1.493(13)
C(1)−C(2)	1.457(16)	1.457(16)	1.495(16)	1.470(11)
C(2)−C(3)	1.546(19)	1.564(20)	1.523(18)	1.544(13)
C(3)−C(4)	1.521(21)	1.517(21)	1.568(20)	1.535(15)
C(4)−C(5)	1.492(21)	1.483(23)	1.483(20)	1.485(15)
C(5)−O(4)	1.437(18)	1.440(19)	1.437(17)	1.438(11)
O(4)−C(1)	1.386(15)	1.397(16)	1.383(15)	1.389(9)
C(1)−O(5)	1.455(18)	1.466(19)	1.477(18)	1.466(11)
O(5)−C(6)	1.419(20)	1.438(20)	1.439(17)	1.431(13)

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Table IV   Compound 7. Fractional coordinates (× 10⁴ for S, P, C and O; × 10³, for H).
Estimated standard deviations in the last digit are given in parentheses.

	x	y	z
S	−2378(2)	1278(2)	387(1)
P	−130(2)	1037(1)	1236(1)
O(1)	874(5)	2313(3)	1715(3)
O(2)	2015(6)	412(3)	872(3)
O(3)	−449(6)	91(3)	2133(2)
O(4)	1791(6)	1495(4)	3652(3)
O(5)	5268(6)	1908(4)	3274(3)
C(1)	3213(8)	2214(5)	3103(4)
C(2)	2936(8)	1961(4)	2029(4)
C(3)	3086(8)	496(5)	1797(4)
C(4)	1648(9)	−250(4)	2471(4)
C(5)	1960(10)	106(5)	3511(4)
C(6)	5941(10)	2194(6)	4237(5)
H(1)	303(8)	312(5)	320(4)
H(2)	410(7)	247(5)	159(4)
H(3)	453(6)	22(4)	182(3)
H(4)	191(9)	−115(6)	238(4)
H(51)	360(6)	−19(4)	374(3)
H(52)	80(11)	−19(7)	405(5)
H(61)	502(9)	165(5)	464(4)
H(62)	546(9)	312(5)	445(4)
H(63)	739(11)	205(6)	416(4)

Table V   Compound 7. Bond lengths in Å and interbond angles in degrees.
Estimated standard deviations in the last digit are given in parentheses.

P–S	1.884(2) Å	SPO(1)	117.5(2)°
P–O(1)	1.608(4)	SPO(2)	121.1(2)
P–O(2)	1.605(4)	SPO(3)	118.1(2)
P–O(3)	1.595(4)	O(1)PO(2)	96.4(2)
C(1)–C(2)	1.527(8)	O(1)PO(3)	103.0(2)
C(1)–O(4)	1.403(7)	O(2)PO(3)	96.5(2)
C(1)–O(5)	1.381(7)	PO(1)C(2)	106.9(3)
C(2)–O(1)	1.444(7)	PO(2)C(3)	96.0(3)
C(2)–C(3)	1.544(7)	PO(3)C(4)	106.1(3)
C(3)–O(2)	1.462(7)	C(2)C(1)O(4)	111.5(4)
C(3)–C(4)	1.525(8)	C(2)C(1)O(5)	104.0(4)
C(4)–O(3)	1.472(7)	O(4)C(1)O(5)	114.3(4)
C(4)–C(5)	1.505(8)	C(1)C(2)O(1)	111.1(5)
C(5)–O(4)	1.446(7)	C(1)C(2)C(3)	111.3(4)
C(6)–O(5)	1.438(8)	O(1)C(2)C(3)	103.8(4)
		C(2)C(3)O(2)	102.2(4)
		C(2)C(3)C(4)	108.9(5)
		O(2)C(3)C(4)	103.0(4)
		C(3)C(4)O(3)	103.9(4)
		C(3)C(4)C(5)	112.8(5)
		O(3)C(4)C(5)	111.8(4)
		C(4)C(5)O(4)	111.1(4)
		C(1)O(4)C(5)	113.4(5)
		C(1)O(5)C(6)	113.7(5)

Structure determination and refinement. The positions of S and P were derived from an (E^2-1)-Patterson synthesis. An eightfold Patterson minimum function based on the positions of the S and P atoms in the unit cell yielded the remaining non-hydrogen atoms. The hydrogen atoms were located in the course of the refinement in a difference Fourier synthesis. Block-diagonal least-squares refinement with anisotropic non-hydrogen and isotropic hydrogen atoms converged to an R value of 3.3%. In the refinement an extinction parameter was included and a weighting scheme $w = 1/(2.5 + F_o + 0.02F_o^2)$ was applied. The anomalous dispersion of S and P was taken into account.
An identical refinement with the inverted structure resulted in an R value of 4.5%. So the original structure apparently represents the correct absolute configuration, in agreement with the known configuration for D-ribose.

The final parameters are listed in Table IV. Bond distances and interbond angles are given in Table V. The atomic numbering is indicated in Fig. 1.

Quantum chemical calculations

From the fractional coordinates for one of the molecules, the deviations in geometry with respect to the other molecules are very small, in the cell of **6**, cartesian coordinates were calculated. The hydrogen atoms which were not resolved in the X-ray analysis were added at fixed distances (0.109 nm) from the appropriate carbon atoms; the normal tetrahedral bond angles were used.
In Table VI some calculated net charges are compared for compounds **4**, **5**, and the triester of methyl β-D-ribopyranoside (**6**).

Discussion

As is evident from Table VI, the differences in charge on the oxygen atoms are only small (it is noteworthy, however, that the charge densities on O(1) and O(3) are different in the case of the ribopyranoside derivative. This is probably due to the methoxy substituent on position C(1)). The calculated charge on the phosphorus atom is rather sensitive to changes in bond angles about this atom. Nevertheless, the trend in phosphorus charge density is confirmed by the fact that the positive charge on phosphorus in **6** is higher than in **4** because of increase in molecular constraint.
No calculations have been performed on compound **7**. However, it is expected that the polarizing ability of the P=S bond certainly makes a comparison of the crystal data for **7** accessible with calculated values for related phosphite species. The earlier calculations[1] on the protonated phosphites **1**–**5** clearly showed that the proton induces enlargement of the OPO angles; consequently, the ring POC angles would decrease[1,2]. Therefore, it is noteworthy to stress that the crystal data for **7** in comparison with **6** perfectly fit into this generalized concept (see Table VII). Apparently, the polarizing tendency of the P=S bond is well mimicked by the phosphorus-protonated phosphites.

Table VI   Calculated net charges (electron units) in compounds **4, 5** *and* **6**.

Compound	P	O(2)	O(1)	O(3)
4ᵃ	0.41	−0.28	−0.28	−0.28
5ᵃ	0.48	−0.30	−0.28	−0.28
6	0.42	−0.29	−0.27	−0.28

ᵃ See ref. 1.

Table VII   Relevant angles in the constraint part of compounds **6** *and* **7**.

Angle	6	7
PO(1)C(2)	110.5	106.9
PO(3)C(4)	107.6	106.1
PO(2)C(3)	97.0	96.0

² A. C. Bellaart, H. M. Buck, P. A. Leclercq and L. J. M. van de Ven, Recl. Trav. Chim. Pays-Bas **96**, 293 (1977).

In a previous paper[2] the suggestion was made that in the phosphite triester **6** the geometry of the ribopyranoside ring would deviate from the chair configuration. The crystal data now clearly show that the chair configuration is still maintained. A similar situation is established for **7**. Still there is one interesting difference which is visualized in the deviation of the angles of the ribopyranoside ring with respect to the normal tetrahedral angles. In compound **7** this deviation is less pronounced than in **6**.

Experimental

Phosphite triester of methyl β-D-ribopyranoside (6)[2,6]

A mixture of methyl β-D-ribopyranoside (49.2 g = 0.3 mol), trimethyl phosphite (40.9 g = 0.33 mol) and triethylamine (3 drops) was heated with stirring for 48 h in a 150 ml flask equipped with a Vigreux column, condenser, receiver, and a drying tube filled with phosphorus pentoxide. During this period methanol (29 g = 0.9 mol) was collected.

The residue was distilled *in vacuo*. Yield: 54 g (0.281 mol = 94 %) of the phosphite triester of methyl β-D-ribopyranoside, b.p. 82–84°C/0.1 mm. It has been crystallized from sodium-dried hexane: colourless needles, m.p. 34.5–35°C.

Thiophosphate O,O,O-triester of methyl β-D-ribopyranoside (7)

A mixture of the phosphite triester of methyl β-D-ribopyranoside (8 g = 0.411 mol) and sulphur (1.32 g = 0.0412 mol) was heated in a Carius tube at 170–175°C. The product was shaken with ether (300 ml) and decolourizing carbon (0.3 g) and filtered. The filtrate was evaporated to 75 ml whereupon a nearly colourless compound (4.7 g) crystallized. From the mother liquor another 0.5 g was obtained. The product was recrystallized from ether using some decolourizing carbon. Yield: 5.0 g (0.022 mol = 54 %) of colourless crystals, m.p. 101–101.5°C. $C_6H_9O_5PS$ (224.18): calcd. C, 32.15; H, 4.05; found C, 32.4; H, 4.1.

Phosphate triester of methyl β-D-ribopyranoside (8)[4,5]

An ozone-oxygen stream* (dried beforehand with Drierite and calcium chloride) was passed into a solution of the phosphite triester of methyl β-D-ribopyranoside (4.7 g = 0.024 mol) in dry methylene chloride cooled to −75°C until a slight blue colour of excess ozone was apparent in the solution. The off-gases were passed through a trap containing neutral potassium iodide solution. The reaction mixture was then sparged with nitrogen to carry excess ozone into the trap. The cold solution of the adduct (^{31}P NMR: = −30.5 ppm upfield from H_3PO_4, clearly pointing to a penta-coordinated phosphorus intermediate) was warmed to 20°C over about 1 h.

Evolution of singlet oxygen proceeded smoothly beginning at about −20°C. The phosphate formed was insoluble in methylene chloride and most other solvents. It was collected and dried *in vacuo* at 100–105°C without further purification. Yield: 4.9 g (0.02355 mol = 98 %) of a colourless, crystalline powder decomposing at ~ 190–195°C. $C_6H_9O_6P$ (208.10): calcd. C, 34.63; H, 4.36; found C, 34.4; H, 4.5.

* Oxidation with HgO[3] was not successful.

[3] *L. Keay* and *E. M. Crook*, J. Chem. Soc. 710 (1961).

[4] *Q. E. Thompson*, J. Am. Chem. Soc. **83**, 845 (1961).

[5] *A. P. Schaap*, J. Org. Chem. **40**, 1185 (1975).

[6] *W. S. Wadsworth* and *W. D. Emmons*, J. Am. Chem. Soc. **84**, 610 (1962).

The role of tetraalkylammonium salts in the electro-reduction of ketones. Part II. The reduction of acetophenone in an aprotic environment

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Abstract. A polarographic study of the electro-reduction of acetophenone in dry acetonitrile has revealed that under strictly anhydrous conditions the carbonyl compound can be reduced only if tetraalkylammonium ions are present. The role played by these ammonium ions is discussed. It is concluded that the catalytic effect of the ammonium ions has to be related to an increased polarization of the carbonyl double bond being induced during collision of the ammonium ions with the carbonyl compound. At high ammonium ion concentrations, however, the effect of this catalysis becomes smaller due to preferential adsorption of the ammonium ions on the electrode surface, as a result of which the carbonyl compound is displaced from the direct vicinity of the electrode.

Introduction

In a previous study[1] we have discussed the effect of the presence of tetraalkylammonium ions on the electro-reduction of carbonyl compounds in aqueous media. This study revealed that (a) at its reduction potential the carbonyl

species is not adsorbed on the electrode surface, (b) that at this potential, in the presence of tetraalkylammonium ions,

[1] *W. J. M. van Tilborg, L. J. G. Dekker* and *C. J. Smit*, Recl. Trav. Chim. Pays-Bas, **97**, 321 (1978).