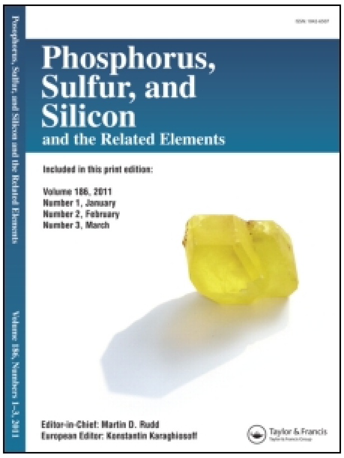

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND STRUCTURES OF 1,2-O-ISOPROPYLIDENE-α-D-GLUCOFURANOSE-3,6-O-CYCLOPHOSPHATE, -THIONO-AND -SELENONOPHOSPHATES

N. S. Magomedova[a]; A. N. Sobolev[a]; V. K. Bel'skii[a]; M. P. Koroteev[ab]; N. M. Pugashova[ab]; E. E. Nifant'ev[ab]
[a] Physico-Chemical Res, Institute by L. Ya. Karpov, ul. Obukha, 10, Moscow [b] Chemistry Department of Moscow, State Pedagogical Institute, Moscow

To cite this Article Magomedova, N. S. , Sobolev, A. N. , Bel'skii, V. K. , Koroteev, M. P. , Pugashova, N. M. and Nifant'ev, E. E.(1991) 'SYNTHESIS AND STRUCTURES OF 1,2-O-ISOPROPYLIDENE-α-D-GLUCOFURANOSE-3,6-O-CYCLOPHOSPHATE, -THIONO-AND -SELENONOPHOSPHATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 3, 261 — 271

To link to this Article: DOI: 10.1080/10426509108038858

URL: http://dx.doi.org/10.1080/10426509108038858

Phosphorus, Sulfur, and Silicon, 1991, Vol. 57, pp. 261–271
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SYNTHESIS AND STRUCTURES OF 1,2-O-ISOPROPYLIDENE-α-D-GLUCOFURANOSE-3,6-O-CYCLOPHOSPHATE, -THIONO- AND -SELENONOPHOSPHATES

N. S. MAGOMEDOVA, A. N. SOBOLEV, V. K. BEL'SKII, M. P. KOROTEEV,* N. M. PUGASHOVA* and E. E. NIFANT'EV*

Physico-Chemical Res. Institute by L. Ya. Karpov, ul. Obukha, 10, Moscow, 103064, USSR

**Chemistry Department of Moscow State Pedagogical Institute, Nesvizsky per. 3, Moscow, 119021, USSR*

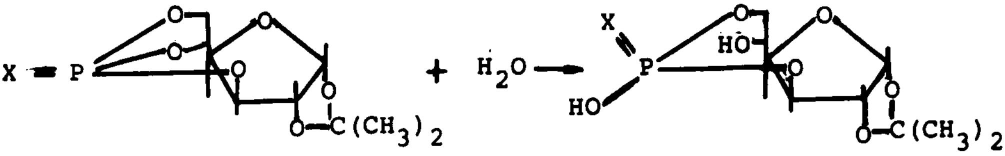
(Received April 24, 1990; in final form July 10, 1990)

3,5,6-Bicyclophosphate of 1,2-O-isopropylidene-α-D-glucofuranose (I), its thiono (II) and selenono (III) analogs undergo unprecedentedly feasible hydrolysis to afford the corresponding 1,2-isopropylidene-α-D-glucofuranose-3,6-cyclophosphate (IV), -thionophosphate (V) and -selenonophosphate (VI). The process is regio- and stereospecific. It occurs with retention of glucose configuration of the monosaccharide backbone and the formation of the phosphepane rings. X-ray structural analysis of the monocyclophosphates formed has been carried out.

Key words: Bicyclophosphate; cyclophosphate, -thiono and -selenophosphate; hydrolysis; X-ray analysis.

We have demonstrated that 1,2-O-isopropylidene-α-D-glucofuranose-3,5,6-bicyclophosphate (I), as well as its thiono (II) and selenono (III) analogs, have a high hydrolytic lability.[1] They transform into two substituted monobasic phosphoric acids even in the presence of traces of moisture. In this respect the above mentioned derivatives display higher reactivity than the derivative of P(III), namely, 1,2-O-isopropylidene-α-D-glucofuranose 3,5,6-bicyclophosphite.

The hydrolysis of I–III is also of interest since in all cases it provides only one novel compound, i.e., the reactions are regio- and stereospecific.[2] The hydrolysis products, 1,2-O-isopropylidene-α-D-glucofuranose-3,6-cyclophosphate (IV), -thionophosphate (V) and -selenonophosphate (VI), refer to poorly investigated compounds of dioxaphosphepane saccharides. There is another observation which is worth mentioning. The glucose configuration of the monosaccharide backbone remains unchanged in all compounds obtained.



I —*III*   *IV*—*VI*   X=O,S,Se

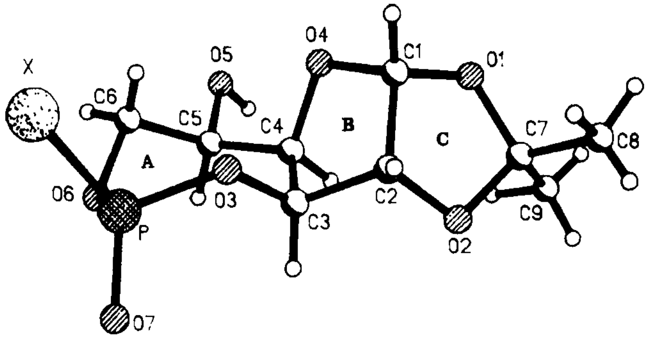


FIGURE 1 A general view of molecules IV–VI.

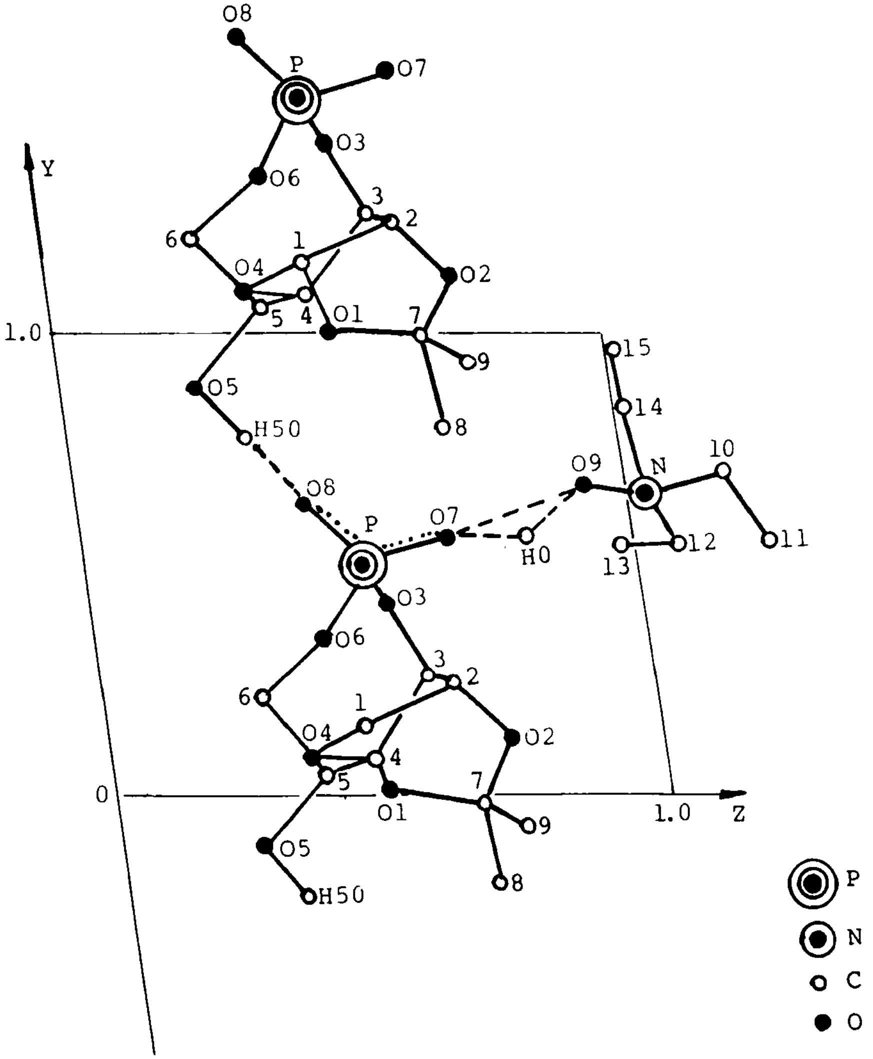


FIGURE 2 (a) A projection of the crystal structure of IV on the plane (100); (b) projections of the crystal structures of V and VI on the plane (001).

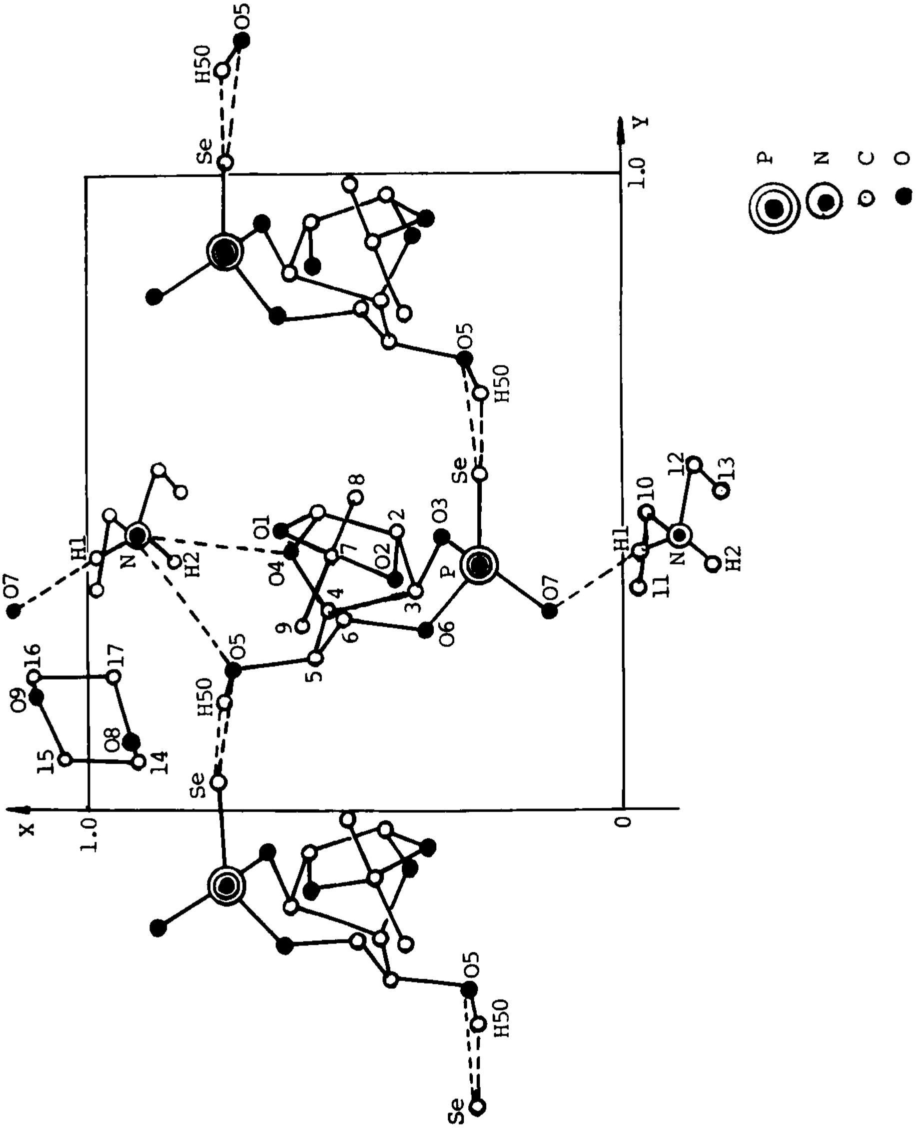

X
1.0
0
Y
1.0
Se
H50
O5
O7
H1
N
H2
O1
O2
O3
O4
O6
O8
O9
P
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
P
N
C
O

FIGURE 2 (b)

One can thus conclude that the P—O rather than O—C bond is hydrolytically broken. The cleavage of the O—C bonds was reported for other phosphates.[3]

The structure of novel cyclophosphorylated glucose derivatives and their typical features have been investigated by X-ray structural analysis. Monocrystals of IV–VI were obtained from dioxane as triethylammonium oxide (IV) or diethylamine (V, VI) salts. The compounds V and VI which besides being isostructural are also isolated as solvates.

Figures 1 and 2 (a and b) show general views of molecules IV–VI and their location in unit cells. Tables I–V contains main crystallographic data, bond lengths and angles. Both, the molecular structure and intra-/intermolecular interactions in the crystal IV differ from those observed in compounds V and VI.

Saturated five-membered heterocycles usually adopt either an envelope conformation with four co-planar atoms or a twist conformation (three atoms are in the plane and two are deflected from the plane in opposite directions).[4]

The 1,3-dioxolane fragment of IV (C) (Figure 1) has an envelope conformation since the O2 oxygen deviates from the mean (± 0.001 Å) plane of four atoms by 0.003 Å, and the angle between the C1, C2, C7, O1 and C2, O2, C7 planes is equal to 158.6°. A similar conformation was observed in 1,2-O-isopropylidene-D-glucofuranose,[5] 4-phenyl-4-benzoyl-1,3-dioxolane[6] and 1,2-O-isopropylidene-α-D-glucofuranose-3,5,6-bicyclophosphite.[7] However, it should be pointed out that when 1,3-dioxolane fragments are condensed with five-membered heterocycles, the carbon atom located between two oxygen atoms deviates from the plane consisting of 4 atoms more often than oxygen.[8,9,10]

Atoms O2 and C7 in V and VI are positioned on opposite sides of the O1, C1, C2 plane. The absolute values of the deviation are similar and equal to: O2 −0.191 Å, C7 +0.232 Å (V) and O2 −0.187 Å, C7 +0.194 Å (VI). Consequently, there is a $^{C7}T_{O2}$ twist conformation in both cases. Thus this is the main conformational

TABLE I

Basic crystallographic data

	IV	V	VI
Formula of the compound	$C_{15}H_{30}O_9NP$	$C_{17}H_{34}NO_9PS$	$C_{17}H_{34}NO_9PSe$
Molecular weight	399	458	505
Space group	P1	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.570 (1)	9.500 (2)	9.536 (2)
b (Å)	7.605 (1)	11.132 (3)	11.222 (3)
c (Å)	9.274 (1)	22.210 (5)	22.279 (7)
alpha (°)	98.22 (1)	90	90
beta (°)	110.28 (1)	90	90
gamma (°)	95.13 (1)	90	90
V (Å^3)	490.0 (2)	2349 (1)	2384 (1)
Z	1	4	4
Number of reflections with I > 3 sigma (I)	1173	1225	1589
R	0.052	0.040	0.025
R_w	0.057	0.040	0.027

TABLE II

Bond lengths (Å) in compounds IV, V and VI (1, 2, 3, rows)

P—O(3) (IV)	1.598 (6)	P—O(6) (IV)	1.564 (5)
(V)	1.609 (4)	(V)	1.590 (4)
(VI)	1.616 (3)	(VI)	1.597 (4)
S—P	1.955 (2)	Se—P	2.110 (2)
P—O(7)	1.467 (8)	P—O(8)	1.467 (6)
	1.474 (4)		
	1.483 (5)		
O(1)—C(1)	1.430 (11)	O(1)—C(7)	1.431 (11)
	1.393 (7)		1.419 (9)
	1.394 (7)		1.426 (7)
O(2)—C(2)	1.427 (11)	O(2)—C(7)	1.431 (11)
	1.402 (7)		1.403 (9)
	1.433 (8)		1.413 (8)
O(3)—C(3)	1.449 (8)	O(4)—C(1)	1.430 (8)
	1.430 (7)		1.430 (7)
	1.440 (6)		1.414 (8)
O(4)—C(4)	1.446 (10)	O(5)—C(5)	1.418 (7)
	1.440 (7)		1.411 (7)
	1.450 (7)		1.425 (6)
O(6)—C(6)	1.454 (11)	C(1)—C(2)	1.528 (13)
	1.441 (8)		1.534 (9)
	1.449 (6)		1.530 (10)
C(2)—C(3)	1.512 (11)	C(3)—C(4)	1.519 (7)
	1.522 (8)		1.508 (9)
	1.537 (8)		1.518 (7)
C(4)—C(5)	1.521 (8)	C(5)—C(6)	1.493 (10)
	1.518 (9)		1.514 (8)
	1.522 (7)		1.504 (7)
C(7)—C(8)	1.486 (12)	C(7)—C(9)	1.518 (11)
	1.516 (12)		1.512 (12)
	1.497 (11)		1.498 (11)
O(9)—N(1)	1.395 (19)	O(9)—O(10)	0.935 (21)
O(9)—N(2)	1.396 (20)		
N(1)—C(10)	1.628 (19)	N(1)—C(12)	1.469 (25)
	1.473 (9)		1.487 (9)
	1.483 (7)		1.469 (7)
C(10)—C(11)	1.342 (38)	C(12)—C(13)	1.528 (25)
	1.477 (11)		1.504 (11)
	1.486 (10)		1.486 (9)
C(14)—C(15)	1.506 (272)	N(1)—C(14)	1.500 (20)

Molecule of 1,4-dioxane (compounds V and VI)

O(8)—C(14) (V)	1.413 (13)	O(8)—C(17) (V)	1.389 (13)
(VI)	1.414 (8)	(VI)	1.390 (9)
O(9)—C(16)	1.438 (15)	O(9)—C(15)	1.387 (18)
	1.406 (10)		1.424 (11)
C(14)—C(15)	1.511 (21)	C(16)—C(17)	1.439 (21)
	1.493 (12)		1.457 (15)

Molecule of triethylammonium oxide (2) (compound IV)

O(9)—C(24)	1.408 (24)	N(1)—O(10)	1.484 (20)
N(1)—C(20)	1.449 (25)	N(1)—C(22)	1.594 (23)
N(1)—C(24)	1.443 (30)	C(10)—C(20)	1.172 (32)
C(10)—N(2)	1.586 (20)	C(11)—C(20)	1.544 (41)
C(10)—C(21)	1.373 (36)	C(12)—N(2)	1.480 (25)
C(12)—C(20)	1.532 (24)	C(12)—C(22)	1.561 (25)
C(12)—C(23)	1.527 (27)	C(13)—C(22)	1.380 (28)
C(14)—C(22)	1.501 (23)	C(14)—N(2)	1.520 (21)

TABLE II (*Continued*)

C(14)—C(25)	1.516 (278)	C(14)—C(24)	1.499 (31)
O(10)—N(2)	1.492 (21)	C(15)—C(24)	1.541 (248)
N(2)—C(22)	1.632 (24)	N(2)—C(20)	1.417 (26)
C(20)—C(21)	1.570 (39)	N(2)—C(24)	1.443 (31)
C(24)—C(25)	1.529 (251)	C(22)—C(23)	1.409 (29)

TABLE III

Bond angles (deg.) in compound IV, V and VI (1, 2, 3 rows)

O(3)—P—O(8)	105.6 (3)	O(6)—P—O(8)	110.8 (4)
S—P—O(3)	104.8 (2)	S—P—O(6)	113.0 (2)
Se—P—O(3)	104.1 (1)	Se—P—O(6)	112.7 (2)
O(7)—P—O(8)	117.3 (5)	O(3)—P—O(7)	111.6 (4)
S—P—O(7)	119.0 (2)		111.9 (2)
Se—P—O(7)	118.8 (2)		112.5 (2)
O(3)—P—O(6) (IV)	104.3 (3)	O(6)—P—O(7)	106.5 (5)
(V)	103.0 (2)		104.2 (2)
(VI)	103.2 (2)		104.6 (3)
C(1)—O(1)—C(7)	110.2 (7)	C(2)—O(2)—C(7)	109.8 (7)
	109.2 (5)		108.5 (5)
	109.5 (4)		107.4 (5)
P—O(3)—C(3)	122.3 (5)	C(1)—O(4)—C(4)	106.9 (6)
	122.1 (4)		107.5 (4)
	121.7 (3)		106.6 (5)
			110.0 (6)
P—O(6)—C(6)	121.0 (6)	O(1)—C1)—O(4)	110.2 (5)
	120.4 (4)		110.3 (5)
	120.0 (3)		107.0 (7)
O(1)—C(1)—C(2)	105.6 (7)	O(4)—C(1)—C(2)	105.4 (5)
	105.2 (5)		106.8 (5)
	105.5 (5)		109.5 (7)
O(2)—C(2)—C(1)	104.2 (7)	O(2)—C(2)—C(3)	110.4 (5)
	104.3 (5)		109.0 (5)
	104.1 (5)		104.8 (6)
C(1)—C(2)—C(3)	103.5 (6)	O(3)—C(3)—C(2)	104.5 (4)
	103.8 (5)		103.8 (4)
	103.5 (5)		101.2 (6)
O(3)—C(3)—C(4)	112.3 (5)	C(2)—C(3)—C(4)	100.8 (5)
	112.7 (5)		100.4 (4)
	112.3 (4)		110.7 (5)
O(4)—C(4)—C(3)	102.5 (5)	O(4)—C(4)—C(5)	108.9 (5)
	101.6 (5)		109.2 (4)
	101.8 (4)		110.6 (5)
C(3)—C(4)—C(5)	120.0 (5)	O(5)—C(5)—C(4)	110.3 (5)
	121.3 (5)		109.6 (4)
	120.5 (4)		113.8 (5)
O(5)—C(5)—C(6)	107.6 (5)	C(4)—C(5)—C(6)	115.6 (5)
	108.0 (5)		116.4 (4)
	107.0 (4)		105.7 (6)
C(6)—C(6)—C(5)	107.9 (6)	O(1)—C(7)—O(2)	106.0 (5)
	108.8 (5)		105.4 (4)
	108.3 (4)		110.2 (8)
O(1)—C(7)—C(8)	108.3 (7)	O(2)—C(7)—C(8)	111.5 (7)
	108.6 (6)		111.3 (6)
	109.2 (5)		109.9 (6)
O(1)—C(7)—C(9)	108.9 (8)	O(2)—C(7)—C(9)	108.5 (6)
	108.2 (6)		108.0 (6)
	108.4 (6)		

TABLE III (*Continued*)

C(8)—C(7)—C(9)	113.4 (7)		
	113.7 (6)		
	114.1 (6)		
Molecules of diethylammonium and 1,4-dioxane (compounds V and VI)			
N—C(10)—C(11) (V)	111.6 (6)	O(9)—C(15)—C(14) (V)	110.7 (12)
(VI)	111.6 (5)	(VI)	110.2 (7)
C(10)—N—C(12)	112.7 (5)	C(16)—O(9)—C(15)	107.3 (10)
	113.6 (4)		108.9 (6)
N—C(12)—C(13)	111.8 (6)	O(9)—C(16)—C(17)	110.4 (11)
	112.2 (5)		111.1 (8)
C(14)—O(8)—C(17)	107.7 (8)	O(8)—C(17)—C(16)	112.3 (10)
	109.2 (5)		111.2 (7)
O(8)—C(14)—C(15)	108.5 (10)		
	109.2 (6)		

distinction between this structural fragment in the phosphate (IV) and thiono- (V) and selenonophosphates (VI). Endocyclic angles of cycles C of IV–VI are similar but there are substantional differences in bond distances of chemically equivalent C—O bonds. This effect manifests itself in structures V and VI since in IV the C—O bonds are practically equal.

A tentative explanation of this fact may be based on an assumption that in IV–VI an envelope conformation of the 1,3-dioxolane fragment is more energetically favorable than a twist conformation, since in these structures the atoms of the fragment are not involved in strong intra- and intermolecular interactions which may affect a conformation. The assumption is supported by a symmetrical composition of the 1,3-dioxolane cycle in its envelope conformation.[8,9,10]

The furanose ring B, likewise all related compounds[5,7,8,9,11] is nonplanar. The C4 atom deviates from the plane of four atoms (IV 0.615 Å, V 0.647 Å, VI 0.652 Å) forming an "envelope" with the bending angles of 138.6, 136.1 and 135.9° for IV–VI respectively. The four-atom fragment O4, C1, C2, C3 is less planar in IV (±0.057 Å) as compared with V (±0.042 Å) and VI (±0.025 Å) and less symmetrical with respect to the line that binds the C4 atom and the midpoint of the C1—C2 bond. The latter is seen from the difference in the torsion angles C1—C2—C3—C4 and C4—O4—C1—C2 which are equal to: IV 31.9 and −17.9°, V 31.4 and −21.8°, VI −29.3 and −24.1°. Besides, the torsion angle O4—C1—C2—C3, i.e., the angle between O4—C1 and C2—C3 bonds, is equal to 9.8, 7.1 and 4.5° in IV–VI, respectively. It seems likely that the oxygen of the saturated furanose cycle in IV which is not involved in molecular interactions possesses higher mobility than in V and VI.

The bond distances and angles of the fragment B in IV–VI do not deviate considerably and are close to the standard values ($C_{sp}3$—O_{av} 1.442 Å, $C_{sp}3$—$C_{sp}3$ 1.530 Å).[12]

The BC fragment has a distorted "butterfly" configuration. The five-membered rings in IV have an envelope conformation, and the C4 and O2 atoms are bended towards the inner part of the butterfly providing an endo-endo conformation of the bicycle with a dihedral angle of 122.3° (in V and VI the angles between the planes of O4, C1, C2, C3 and O1, C1, C2 are equal to 119.8 and 120.3°, respectively).

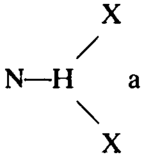
The dioxaphosphepane fragment A in all three structures has a conformation of an asymmetrically distorted "chair P(σ)",[12] since its best plane consists of O3, C3, C5, C6 atoms (IV ±0.022 Å, V and VI ±0.063 Å). Atoms C4 deviate from the plane 0.562, 0.512 and 0.528 Å in the cases IV–VI, respectively, while atoms P and 06 deviate −1.125 and −1.203 Å (IV), −1.055 and −1.209 Å (V), −1.071 and −1.222 Å (VI) correspondingly. The lack of symmetry with respect to the line binding C4 and the midpoint of the P—06 bond is supported by the difference in torsion angles C4—C5—C6—O6 and C4—C3—O3—P (−79.9 and −85.6° IV, −72.5 and −87.5° V, −73.6 and −87.9° VI). In the four-atom fragment O3, P, O6, C6 deviations of atoms from the mean plane are the following: P 0.148, O6 −0.170, O3 −0.074, C6 −0.096 Å in IV, P 0.177 (0.178), O6 −0.208 (−0.208), O3 −0.088 (−0.089), C6 0.119 (0.119) Å in V (and VI). The best planes make up the following angles with the four-atom fragments 58.4° (IV), 56.7° (V) and 57.4° (VI), while with the three-atom fragments the angales are 47.8°, 44.9° and 44.6°. The tetracoordinated phosphorus atom stands apart from the plane O3, O6, C6 by 0.435 Å in IV (by 0.530 Å in V and VI) and from the plane of three oxygens by 0.561 Å (IV), 0.591 Å (V) and 0.585 Å (VI). The substituents at phosphorus (O8, S, Se) are in a pseudo-equatorial position with respect to the best plane deviating from the latter by −0.630 Å (IV), −0.257 Å (V), and −0.202 Å (VI). The atoms O7 occupy pseudoaxial positions and their deviations are −2.435 Å (IV), −2.381 Å (V) and −2.406 Å (VI).

The distances of the cyclic P—O bonds fall in the range of mean values (1.58–1.61 Å)[12,13] but the somewhat shortened P—O6 bond in IV (1.564 Å) is similar to that observed in tetramethylenephosphoric acid (1.556 Å).[14] A decrease in the internal bond angle at C5 (113.8°) is seen in IV, if compared with V and VI (115.6 and 116.4° respectively). Other endocyclic angles, bond distances C—O and C—C show a minor variation. But if compared with tetramethylenephosphoric acid, the bond distances C3—C4 and C4—C5 of which are equal to 1.504 Å, while the angle C3—C4—C5 is 115.7°, one can notice the lengthening of these bonds (av. 1.518 Å) and an increase in the bond angle at C4 up to 120.6° (av.). These discrepancies can be rationalized in terms of different conformations of their seven-membered cycles: the acid molecule[14] is symmetrical with respect to the line between P and C4—C5 bond.

The P=X bonds (P=O 1.467 Å, P=S 1.955 Å, P=Se 2.110 Å) are somewhat longer than the standard values (P=O 1.449 Å, P=S 1.922 Å, P=Se 2.093 Å)[12] due to involvement of these functions in intermolecular contacts. One can see in Figure 2 (a, b) that the hydroxyl hydrogens (O5H5o) are directed towards O, S and Se atoms. Hydrogen bonds are thus formed in IV (O5H5o . . . O8) uniting translationally identical molecules. In V and VI the H-bonding is realized between molecules which are bound by the second-order screw axis.

Despite H . . . S bonds, as well H . . . Se ones, which are poorly investigated, it is known[15,16] that their geometry may be typical of the hydrogen bonds of medium strength. The S . . . H bond reported is approximately linear and has the following characteristics: O . . . S 3.19–3.55 Å, H . . . S 2.25–2.59 Å, O—H . . . S angle[16] 153–180°. In the crystals investigated these values are: O . . . S (Se) 3.308 (3.401)

Å, H . . . S (Se) 2.53 (2.59) Å, angle O—H . . . S (Se) 161 (166)°. A small increase in the P═S and P═Se bonds mentioned above is also indicative of the intermolecular interactions of medium strength. A slight shortening (i.e., strengthening) of the H-bond in IV compared with V and VI (O5H5o . . . O8 2.675 Å, H5o . . . O8 1.71 Å, angle O5–H5o . . . O8 145°; standard OH . . . O 2.72 Å)[17] can be accounted by the following: in IV, contrary to V and VI, the hydroxyl O5 is bound with P═O8 only while O4 is not involved in intermolecular interactions (in V and VI O5 and O4 oxygens forms bifurcate bonds with the amino group of diethylammonium).

Interatomic distances of the three-centered bifurcate bonds  $\text{N—H}\begin{array}{l} / \text{X} \\ \backslash \text{X} \end{array}$ are usually longer than the corresponding distances of the linear N—H . . . X bonds[18] (N . . . O 2.89–2.94 Å,[17] H . . . O 1.90 Å).[18] The bifurcate bonds in V (and VI) can be treated as middle-strength bonds, since their geometric parameters do not significantly differ from those of linear NH . . . O bonds (NH2 . . . O4 2.951 (2.951) Å, NH2 . . . O5 2.972 (2.988) Å, angle N—H2 . . . O4 130 (135)°, angle N—H2 . . . O5 155 (154°). In both cases the hydrogen bonds with O4 are slightly shorter compared with O5, i.e., they are stronger. The second atom of the diethylammonium ion (H1) forms a hydrogen bond with O7. This bond cross-links the molecules, involved in the H-bonding S (Se) . . . H5o (O5), which are located at the second-order screw axis (Figure 2b). The NH1 . . . O7 bond distance in V and VI is shorter than the standard value of 2.89 Å[17] indicating the strength of this interaction (O7 . . . H1 (N) 1.83 Å, O7 . . . N 2.695 Å, N—H1 0.88 Å, angle O7 . . . H1—N 166° in V; 1.93 Å, 2.723 Å, 0.78 Å, and 176° in IV).

The O7 atom in IV is bound with triethylammonium oxide (O7 . . . Ho . . . O9, Ho . . . O7 1.31 Å, Ho . . . O9 1.30 Å, O7 . . . O9 2.520 Å, angle O7 . . . Ho . . . O9 150°) and the hydrogen bond thus formed is obviously as strong as that for O7 in V and VI, since the difference between the standard values of N . . . O and O . . . O bonds is approximately constant and equal to ca. 0.2 Å in all structures. Interatomic distances P—O7 and P—O8 in IV are equal (1.467 A) and close within experimental limits to the standard values (1.483 A) of the systems with delocalized P . . . O bonds.[12] Similar averaging of the bonds (1.486 and 1.473 Å) was observed for 2,5-arabinosylcytidine monophosphate,[11] whereas in molecules with localized bonds the values of interatomic distances are different (P═O 1.472 Å, P—OH 1.522 Å[14] and P═O 1.455 Å, P—OPh 1.574 Å).[19] Averaged P═O bonds vary in the range 1.44–1.48 Å,[12] while P—OR bonds are in the range of 1.510–1.582 Å.[20] All these observations suggest the formation of O8 . . . P . . . O7 moiety with the delocalized formal negative charge. Atoms O7 and O8, however, form hydrogen bonds of different strength. This is supported not only by their length (O5 . . . O8 2.676 Å, O7 . . . O9 2.520 Å), but also by relatively strong shortening of the P—O7 bond accompanied by less pronounced increase in the P═O8 compared with tetramethylenephosphoric acid[14] (by analogy taking into account a similarity of crystal and molecular structures, the considerations about the delocalization in the O . . . P . . . X fragment may be applied to compounds V and VI).

Consequently, the chain of intermolecular hydrogen bonds in IV with a formal charge distribution can be written as follows: $\bar{O}5\text{–}\overset{+}{H}5O \ldots O8 \, \underline{\ldots} \, \bar{P} \, \underline{\ldots} \, O7 \ldots \overset{+}{H}O \ldots \bar{O}9 \leftarrow \overset{+}{N}$, i.e., the hydroxy group donates hydrogen to the negatively charged O—P—O group, while HO is located at equal distances between O7 and O9 (1.30 Å). Moreover, the interatomic distance N1—O9 in IV is closer to that in trimethylaminooxide ($(CH_3)_3\overset{+}{N} \rightarrow \bar{O}$ 1.388 Å)[21] in which oxygen bears a formal negative charge than to that in trimethylaminooxide hydrochloride ($(CH_2)_3\overset{+}{N} - OH.\bar{C}1$) in which oxygen is a proton carrier and the N—O distance is equal to 1.425 Å.[22]

Nitrogen atoms of the diethylammonium (V and VI) and triethylammonium oxide (IV) are tetrahedral. Geometric characteristics of the diethylammonium ion are quite common. Atoms of trietylammonium oxide are statistically ordered in two equivalent positions.

In principle, the solvating dioxane molecule having a usual chair conformation is as that reported[23]: C—O 1.410 Å, C—C 1.486 Å, angle C—O—C 109.5° and O—C—C 111.1°.

In conclusion, a comparative analysis of crystal and molecular structures of closely related compounds has shown that in IV (O-analogue) translationally identical saccharide molecules are bound with each other and triethylammonium oxide through the O8 $\underline{\ldots}$ P $\underline{\ldots}$ O7 moiety. In crystals V and VI (S- and Se-derivatives) the saccharide molecules are united with P—X . . . H5OO5 hydrogen bonds through the 2_1 axes, while the binding of translationally identical molecules is realized at the expense of H-bonds of the O4, O5 and O7 atoms with hydrogen atoms of the diethylammonium ion.

The furanose and 1,3 dioxolane rings of IV are not involved in intermolecular interactions, thus making the rings more flexible but the bond lengths and angles closer to the standard ones.

EXPERIMENTAL

Crystallographic data for IV–VI were collected on an automatic diffractometer Nicolet P3 (λMoK_α radiation, $\theta/2\theta$ scanning); $2\theta_{(max)}$ = 45° (IV), 48° (V) and 45° (VI).

The structures were solved by direct method and refined by the SHELXTL routine with anisotropic (P, O, N, C) and isotropic (H) parameters and the weighting scheme $\omega = 1/\sigma^2 |F|$.[24] Hydrogen atoms were localized from the difference syntheses, their positional and thermal parameters were included in the final refinement (main crystallographic data and atomic coordinates are summarized in the Tables).

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