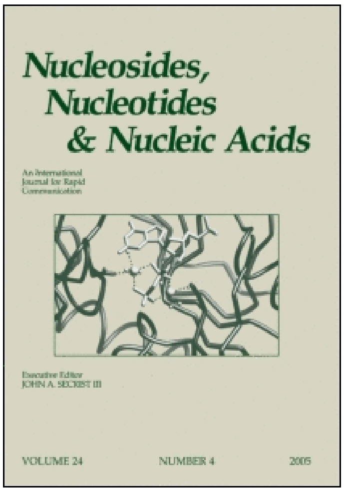

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Cytidinium H-Phosphonate Monohydrate, *bis* 2'-Deoxycytidinium H-Phosphonate and 2'-Deoxycytromium H-Phosphonate -Structures and Properties

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CYTIDINIUM H-PHOSPHONATE MONOHYDRATE, BIS 2'-DEOXYCYTIDINIUM H-PHOSPHONATE AND 2'-DEOXYCYTIDINIUM H-PHOSPHONATE - STRUCTURES AND PROPERTIES

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ABSTRACT: The crystal structures of cytidinium H-phosphonate monohydrate, bis 2'-deoxycytidinium H-phosphonate and 2'-deoxycytidinium H-phosphonate have been determined by single crystal X-ray diffraction and FTIR spectroscopy. The influence of protonation and hydrogen bond formation on geometry of the cytidine fragment has been studied. All three compounds have similar geometry and conformation but they form different H-bond networks. Contrary to the phosphates of cytidine and deoxycytidine, the phosphonates do not form direct base pairs but they strongly interacts with H_3PO_3 acid and/or its anions present in the crystal lattice. This seems to be more favourable than the base-base interactions. As a result a pleated sheets are formed consisting from alternating columns of the cations and anions. The sheets are joined by additional O-H...O=P bonds giving a 3D network.

Cytidine, 2'-deoxycytidine and their derivatives form a significant group of compounds in organic chemistry and biology being one of the constituents of the nucleic acids, DNA and RNA, - compounds crucial for biological information, transfer and storage. In all these processes the key role is played by hydrogen bonding.

A number of papers has already been published on such structures and related topics. Among others, structural properties of cytidine and 2'-deoxycytidine sulphates have been discussed in ref. 1, mono- and hemi- dihydrogenphosphates in refs. 2 and 3. Isomorphism, solid state transformations, and disorder in the crystal structures of cytidinium and 2'-

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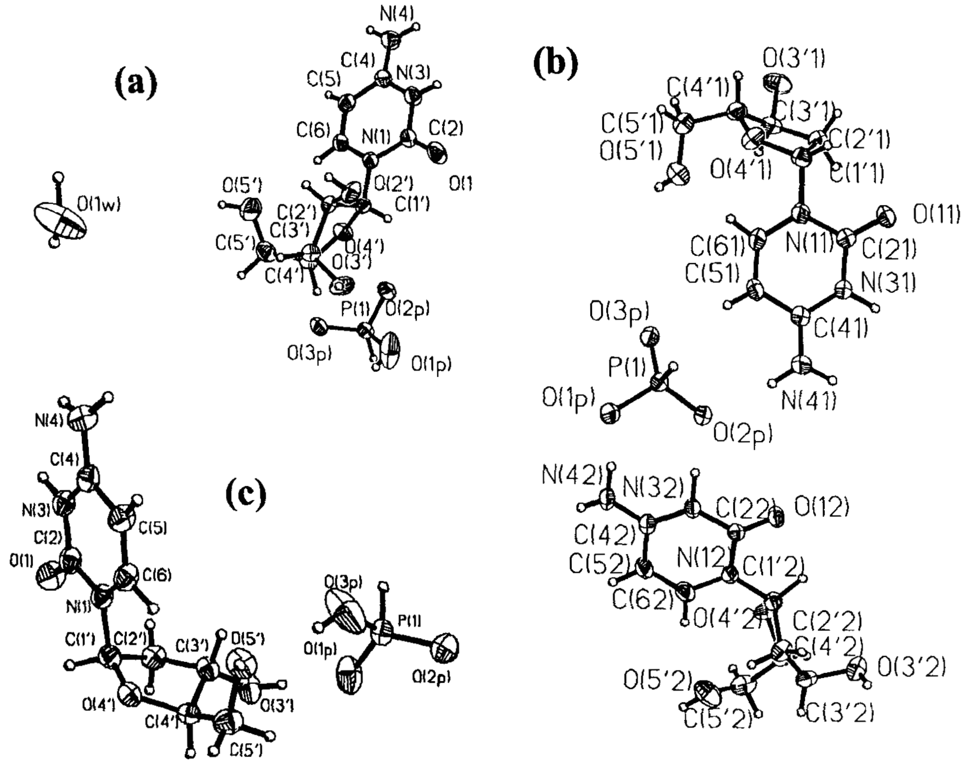

Figure 1. Labelling of atoms and ORTEP illustration of thermal motions of atoms in the complex of cytidinium phosphonate monohydrate (a), bis 2'-deoxycytidinium H-phosphonate (b) and 2'-deoxycytidinium H-phosphonate (c).

deoxycytidinium salts were presented in ref. 4. In the case of hemiprotonated salts, cytosine fragment is capable of forming stable CytH$^+$Cyt units[3,4-12] containing three hydrogen bonds. Such pairs are of crucial importance in the i-DNA structure[13] consisting of two hemi-protonated parallel dCydH$^+$dCyd duplexes running in opposite directions. The hemidihydrogenphosphate salt of 2'-deoxycytidine also contains rather unusual infinite hydrogen bonded $(H_2PO_4^-)_\infty$ columns[3]. One of the aims of this work is to check whether a simpler acid H_3PO_3 can form similar structures of compounds with cytidine and 2'-deoxycytidine as H_3PO_4 does. Protonation effect on parent and chemically modified cytidine nucleosides - achieved with the hydrochloric acid - was also discussed in a number of papers[14-16]. Structures of N-methylated cytidinium chloride and nitrate were also reported[17-18].

This work is also a continuation of a series of structural studies concerning the problem of influence of different counterions and protonation on conformation, electronic and geometrical structure and hydrogen bonding properties of nucleoside cations. The influence of counterions has already been recognized in such areas as conformational transitions in DNA[19] and stabilizing effect on secondary and tertiary structures of nucleic acids[20].

This paper reports new structures of cytidinium H-phosphonate monohydrate, bis 2'-deoxycytidinium H-phosphonate and 2'-deoxycytidinium H-phosphonate and introduces a new interesting anions of H_3PO_3 acid into the discussion of the role of counterions in nucleoside complexes.

EXPERIMENTAL

SYNTHESIS; $CydH^+ \cdot H_2PO_3^- \cdot H_2O$ - Cytidinium H-phosphonate monohydrate was prepared by mixing 2g (8.2mM) of cytidine suspended in 15 ml MeOH with 0.805g (9.8 mM) of H_3PO_3 dissolved in 5 ml MeOH. The mixture was warmed to clear turbidity. Slow crystallization at room temperature led to the first crop (2.5 g) of crystalline product.

Yield 88%; m.p. 93-107°C; Elemental analyses were measured using a Perkin-Elmer model 240. Anal. Calcd for $C_9H_{16}N_3PO_8 \cdot H_2O$, m.w. 343; C, 31.48; H, 5.24; N, 12.24. Found: C, 31.44; H, 4.91; N, 12.11.

From the monohydrate of cytidinium H-phosphonate crystalline water molecules can be removed when the sample is kept over P_2O_5 for 3 days at RT. When dehydrated salt kept over saturated aqueous KCl solution for 24h at RT, it undergoes rehydration process. These processes were observed by FTIR-PAS spectra.

$(dCydH^+)_2 \cdot HPO_3^{2-}$- bis 2'deoxycytidinium H-phosphonate. To 0.7g (3.08 mM) of 2'-deoxycytidine suspended in 3ml of methanol, 0.311g (3.79 mM) of H_3PO_3 dissolved in 1ml of methanol was added (molar eqv. ratio 1:1.2). To obtain homogeneous solution 1.5 ml MeOH was used and the mixture was heated. Slow crystallization at room temperature led to the crystals of bis-2'-deoxycytidinium H-phosphonate from which suitable single crystals were selected for X-ray analysis.

Yield, 84%; m.p. 158-160 C. E.A Calcd for $C_{18}H_{29}N_6PO_{11}$; m.w. 536; C, 40.29; H, 5.41: N, 15.67; found: C, 40.20; H, 5.18; N, 15.36.

$dCydH^+ \cdot H_2PO_3$ - 2'-deoxycytidinium H-phosphonate. An excess of H_3PO_3-anhydro is needed to obtain 2'-deoxycytidinium H-phosphonate. Both substrates, 681 mg (3 mM) of deoxycytidine and 369 mg (4.5 mM) of H_3PO_3 (molar eqv.ratio 1:1.5) were dissolved in methanol. After leaving the mixture at the room temperature for 24 h, 655 mg of 2'-deoxycytidinium and 16 mg of bis-2'-deoxycytidinium were obtained. The recrystallization of

2'-deoxycytidinium H-phosphonate provides bis-2'deoxycytidinium H-phosphonate. To avoid this, some additional amount of H_3PO_3 should be added during recrystallization.

Yield, 71%, m.p. 143-145°C. E.A. Calcd for $C_9H_{16}N_3PO_7$; m.w. 309; C, 34.95; H, 5.17; N, 13.59. Found: C, 35.10; H, 5.20: N, 13.60.

All the salts - described above - can be obtained by applying transformation in the solid state. For example, when crystalline bis-2'-deoxycytidinium H-phosphonate is mixed in the agate mortar with crystalline H_3PO_3 in the molar eqv. 1:1 ratio, crystalline 2'-deoxycytidinium H-phosphonate is obtained. When crystalline 2'-deoxycytidinium H-phosphonate is mixed with the crystalline 2'-deoxycytidine in the molar eqv. (1:1) ratio, bis-2'-deoxycytidinium H-phosphonate is formed. The transformations were followed by FTIR-PAS spectra. The FTIR-PAS spectra of both products were identical with the reference spectra of 2'-deoxycytidinium H-phosphonate and bis-2'-deoxycytidinium H- phosphonate respectively, and gave correct E.A.

The FTIR-PAS spectra were recorded using a BOMEM 152 spectrometer and a photoacoustic cell, model 100 MTEC. The data were Fourier transformed and averaged out after 64 scans at 8 cm^{-1} resolution. All spectra were obtained at room temperature in the region 4000 - 500 cm^{-1}.

X-Ray Diffraction. The X-ray measurements were done on a KM-4 KUMA diffractometer with graphite monochromated CuKα and MoKα radiation. The data were collected at room temperature using ω-2θ scan technique. The intensity of the control reflections varied by less than 3%, and linear correction factor was applied to account for this effect. The data were also corrected for Lorentz and polarization effects, but no absorption correction was applied. The structure was solved by direct methods[21] and refined using SHELXL[22]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The criterion $F_o^2 > 2\sigma(F_o^2)$ was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. R factors based on F^2 are about twice as large as those based on F. All hydrogen atom were located from difference map and refined isotropically. Scattering factors were taken from Tables 6.1.1.4 and 4.2.4.2 in ref. 23. Experimental details concerning the collection and refinement of data are summarised below:

$CydH^+ \cdot H_2PO_3^- \cdot H_2O$. Empirical formula $C_9H_{18}N_3O_9P$, formula weight 343.23, temp.=293(2) K, λ=1.54178 Å, orthorhombic, space group=$P2_12_12_1$, unit cell dimensions:

a=6.648(1) Å, b=14.021(1) Å, c=15.102(1) Å, Z=4, μ=2.261 mm^{-1}, F(000) = 720, crystal size = 0.20x0.30x0.25 mm^3, independent reflections = 1968 [R(int) = 0.056], data/restraints/parameters = 1946/0/272, goodness-of-fit on F^2 = 1.083, final R indices [I>2σ(I)]: R1=0.0445, wR2=0.1096, R indices (all data): R1=0.0491, wR2=0.1246, absolute structure parameter= -0.02(3), extinction coefficient = 0.024(2), largest diff. peak and hole [eÅ^{-3}]=0.38 and -0.32.

$(dCydH^+)_2 \cdot HPO_3^{2-}$. Empirical formula $C_{18}H_{29}N_6O_{11}P$, formula weight 536.44, temp.= 293(2) K, λ= 0.71073Å, monoclinic, space group C2, unit cell dimensions: a=38.106(1) Å, b=7.401(1) Å, c=8.283(1) Å, β=93.97(1)°, Z=4, μ= 0.191 mm^{-1}, F(000)=1128, crystal size = 0.25x0.30x0.20mm^3, independent reflections = 4104 [R(int) = 0.0435], data/restraints/ parameters = 4047/1/442, goodness-of-fit on F^2 =1.070, final R indices [I>2sigma(I)]: R1 = 0.0312, wR2 = 0.0703, R indices (all data): R1 = 0.0497, wR2 = 0.1727, absolute structure parameter=0.05(9), extinction coefficient=0.0040(4), largest diff. peak and hole [eÅ^{-3}]= 0.18 and -0.16.

$dCydH^+ \cdot H_2PO_3^-$. Empirical formula $C_9H_{16}N_6O_7P$, formula weight 309.22, temp.= 293(2) K, λ=1.54178Å, monoclinic, space group $P2_1$, unit cell dimensions: a=5.329(1)Å, b=11.787(2) Å, c=10.609(2) Å, β=96.93(3)°, Z=2, μ= 2.221 mm^{-1}, F(000)=324, crystal size = 0.30x0.20x0.25mm^3, independent reflections = 1714 [R(int) = 0.0239], data/restraints/ parameters = 1712/1/246, goodness-of-fit on F^2 =1.065, final R indices [I>2sigma(I)]: R1 = 0.0399, wR2 = 0.1037, R indices (all data): R1 = 0.0411, wR2 = 0.1080, absolute structure parameter=0.01(3), extinction coefficient=0.0023(2), largest diff. peak and hole [eÅ^{-3}]= 0.49 and -0.28.

Full X-ray structural data for all compounds have been deposited as Supplementary Materials to this publication.

DISCUSSION

IR - Cationic part. FTIR-PAS spectra of crystalline salts: $CydH^+ \cdot H_2PO_3^- \cdot H_2O$, $CydH^+ \cdot H_2PO_3^-$, $dCydH^+ \cdot H_2PO_3^-$ $(dCydH^+)_2 \cdot HPO_3^{-2}$ show very broad and intense absorption in the range of 3600 - 2600 cm^{-1} in which the stretching vibrations of all kinds of X-H bonds overlap (X=O,N,C). The first set of bands 3600 -3200 cm^{-1} reflects internucleoside or interionic interactions, since they stem from the stretching vibrations of the N-H and O-H bonds which participate in hydrogen bond networks as proton donors. In the case of $CydH^+ \cdot H_2PO_3^- \cdot H_2O$ the stretching vibrations of O-H bonds from water molecule appear at ca.

3563 cm^{-1} and 3486 cm^{-1}. On the basis of X-ray data one can ascribed the first of them to free O-H group from the water molecule, whereas the second one comes from the hydrogen/proton interacting with oxygen atom (O3') from the sugar fragment. Of course in the case of the dehydrated salt such bands are not observed. The second set of bands 3200-2800 cm^{-1} concerns the stretching vibrations of the C-H bonds. The 3200-3000 cm^{-1} band arises from the stretching vibrations of the base C-H bonds, while the set of bands located at lower frequencies (3000 - 2800 cm^{-1}) is connected with the stretching vibrations of sugar C-H bonds. The set of bands in the range 1800 - 1500 cm^{-1} concerns the stretching vibrations of the double C=O, C=N, C=C bonds characteristic for heterocyclic bases sensitive to base interactions. Due to the ν(C2=O2) vibration, strong absorption bands are observed at ca. 1719 cm^{-1} in $CydH^{+}{\cdot}H_2PO_3^{-}{\cdot}H_2O$, ca. 1692 cm^{-1} in $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ and ca. 1704 cm^{-1} in $dCydH^{+}{\cdot}H_2PO_3^{-}$. The carbonyl groups of two positively charged $dCydH^{+}$ fragments in $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ form two hydrogen bonds: one to the O5'H group and the second one to the N4H group. Therefore the carbonyl vibration occurs at a lower frequency in comparison with $dCydH^{+}{\cdot}H_2PO_3^{-}$. It must be noted that the C2=O2 bond lengths in $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ (1,231 Å and 1,219 Å) are longer than the one in $dCydH^{+}{\cdot}H_2PO_3^{-}$(1,208 Å).

The glycosidic bond is localized between C1' and N1 atoms. Absorption bands, shown in Table 1, are due to vibrations of heterocyclic bases coupled to ribose or deoxyribose moieties. The length of C1'-N1 bond is greater than some other C-N distances (The Supplementary Materials Tables 3, 6 and 9). The position of the C1'-N1 band strongly depends on the glycosidic torsion angle (Table 4). Similarly, the frequency of ν(C1'-N1) stretching vibrations, indicates that the investigated compounds have *anti* conformation of the glycosidic bond. This is in a good agreement with the X-ray data (Table 4).

The spectral region between 950 and 800 cm^{-1} contains absorption bands involving vibrations of the sugar moieties coupled to the base vibrations. Several of these bands are extremely conformation sensitive and can be used to characterize the sugar pucker. The observed bands at ca. 859 cm^{-1} for $CydH^{+}{\cdot}H_2PO_3^{-}{\cdot}H_2O$ and $dCydH^{+}{\cdot}H_2PO_3^{-}$ and at ca. 866 cm^{-1} for $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ can be assigned to the δ(C6-N1-C1') and δ(C2-N1-C1') vibrations. In this region conformationally sensitive band of lower frequency at 816 cm^{-1} for $CydH^{+}{\cdot}H_2PO_3^{-}{\cdot}H_2O$ and at 828 cm^{-1} for $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ have been assigned to the δ(C2'-C1'-O4') vibrations which corresponds to C2'- endo geometry of the sugar ring. The band at 843 cm^{-1} for $(dCydH^{+})_2{\cdot}HPO_3^{-2}$ and $dCydH^{+}{\cdot}H_2PO_3^{-}$ corresponds to the C3'-endo ring puckering - in agreement with the X-ray data (Table 4).

TABLE 1. Selected bands observed in FTIR -PAS spectra of studied compounds.

Absorption Bands ν,δ [cm^{-1}]	$CydH^+ \cdot H_2PO_3^-$ $\cdot H_2O$	$CydH^+ \cdot H_2PO_3^-$	$(dCydH^+)_2 \cdot HPO_3^{-2}$	$DCydH^+ \cdot H_2PO_3^-$
ν(C=O)	1719	1723	1692	1704
ν(C2-N1) ν(C6-N1)	1233	1229	1233	1248
ν(C4-N4)	1276	1275	1283	1279
ν(C1'-N1)	1183	1164	1179	1179
δ(C2-N1-C1') δ(C6-N1-C1')	859	859	866	859
δ(C2'-C1'-O4')				
C3'-endo			843	843
C2'-endo	816	824	828	

IR - Anionic part. Vibrations typical for $H_2PO_3^-$, HPO_3^{-2} anions are related to those of P-O, P-OH, PO-H groups. In the spectra of the salts studied, the stretching vibrations ν(PO-H) appear in the similar range to the N-H stretching bands therefore it is difficult to determine their exact positions precisely. Some other vibration types: bending of P-OH and PO-H groups as well as stretching and bending of P-O groups can be found in the 1320-400 cm^{-1} range. The bands originating from the bending vibrations of PO-H; P-OH groups [in plane deformation - δ(PO-H)] can be found in the range from 1320 - 1170 cm^{-1}. Strong stretching vibration bands of P=O and P-O$^{-\delta}$ appear in the range 1164 - 994 cm^{-1}. The P=O stretching vibrations are observed at the higher frequency and two types of P-O$^{-\delta}$ vibrations: degenerate ν(P-O$^{-\delta}$) and symmetrical ν(P-O$^{-\delta}$) are at the lower frequency. The spectra of monohydrate and dehydrated cytidinium H-phosphonate, differ in this region which suggests that dehydration leads to significant changes in the interactions of the $H_2PO_3^-$ residue.

The bands originating from stretching vibrations of P-OH group appear at 913 cm^{-1} for the monohydrate and at 917 cm^{-1} for the dehydrated salt. The bending out-of-plane vibrations of this group are observed in the range 882-816 cm^{-1}, whereas the bands from the bending vibrations of the O-P-O groups are located below 600 cm^{-1}. In all the spectra one sharp band located around 2400 cm^{-1} is observed. It is connected with the stretching vibrations of the P-H bond. For the cytidinium H-phosphonate monohydrate at 2441 cm^{-1}, in the dehydrated salt this band is shifted up to 2417 cm^{-1}, for $dCydH^{+} \cdot H_2PO_3^{-}$ at 2371 cm^{-1} and for $(dCydH^{+})_2 \cdot HPO_3^{-2}$ at 2367 cm^{-1}.

X-ray analysis. The overall view and labelling of atoms in all three phosphonate salts as well as their thermal motions are shown in Fig. 1. Selected bond lengths and valence angles are given in Table 2. The packing arrangement of the molecules in crystals is displayed in Figs. 3-5. The crystal structures of all three compounds are built up from layers of pairs of stacked cations and anions which form - via hydrogen bonds - molecular planes. Cytidinium H-phosphonate monohydrate crystallizes in the orthorhombic $P2_12_12_1$ space group with one molecule in the independent part of the unit cell. The other two molecules crystallize in the monoclinic C2 and $P2_1$ space groups for $(dCydH^{+})_2 \cdot HPO_3^{2-}$ and $dCydH^{+} \cdot H_2PO_3^{-}$, respectively. The coordinates of atoms, the equivalent/isotropic temperature factors as well as the full geometry and anisotropic thermal parameters are given in the Supplementary Materials.

Structural parameters of all three cytosine fragments are consistent - they differ only within the level of errors - and are in a good agreement with other reference structures[2-4] In all cases the value of the C2N3C4 angle is close to 125° which suggests that N3 is protonated.

The pyrimidyne fragment of $CydH^{+} \cdot H_2PO_3^{-} \cdot H_2O$ is planar with only minor deviations from the least-square plane (for N1 and C2 equal to -0.009 Å and 0.007 Å, respectively). In the case of the $(dCydH^{+})_2 \cdot HPO_3^{2-}$ the first pyrimidine ring is quite distorted from planarity with the average deviation of atoms equal to ca. 0.02 Å, whereas the second pyrimidine fragment is really flat with the deviation of atoms equal to ca. 0.003 Å. The third salt $dCydH^{+} \cdot H_2PO_3^{-}$ has its pyrimidine ring similar to the one in the monohydrate.

The $-N4H_2$ group in all these compounds is almost co-planar with the pyrimidine part although the angle between the best planes of these two molecular fragments is equal to 10.2°, 4.4° and 2.2° and 7.1° for $CydH^{+} \cdot H_2PO_3^{-} \cdot H_2O$, $(dCydH^{+})_2 \cdot HPO_3^{2-}$ and $dCydH^{+} \cdot H_2PO_3^{-}$, respectively.

All O-H and N-H groups in $CydH^{+} \cdot H_2PO_3^{-} \cdot H_2O$ are involved in different types of hydrogen bonding (Table 3). In particular the $N3^{+}$-H group forms H-bond to O2 atom from the $CydH^{+}$ moiety related by 1-x, 1/2+y, 1/2-z symmetry. Also the $-N4H_2$ group participates in two strong hydrogen bonds to O1P and O3P atoms from neighbouring $H_2PO_3^{-}$ anions [-x, 1/2+y, 1/2-z and 1-x, 1/2+y, 1/2-z, respectively]. The O-H groups from the sugar fragment (O3'-H3' and O5'-H5') take part in H-bonding to O2P oxygen atom, to (O3'-H3') and to another sugar oxygen atoms (O2' and O3') from the $CydH^{+}$ [x-1,y,z] residue.

The water molecule present in this structure is involved in H-bonding by donating its hydrogens to O3' [1-x, 1/2+y, 1/2-z], O1P, O2' and O5' [1+x,y,z] acceptors atoms at the same

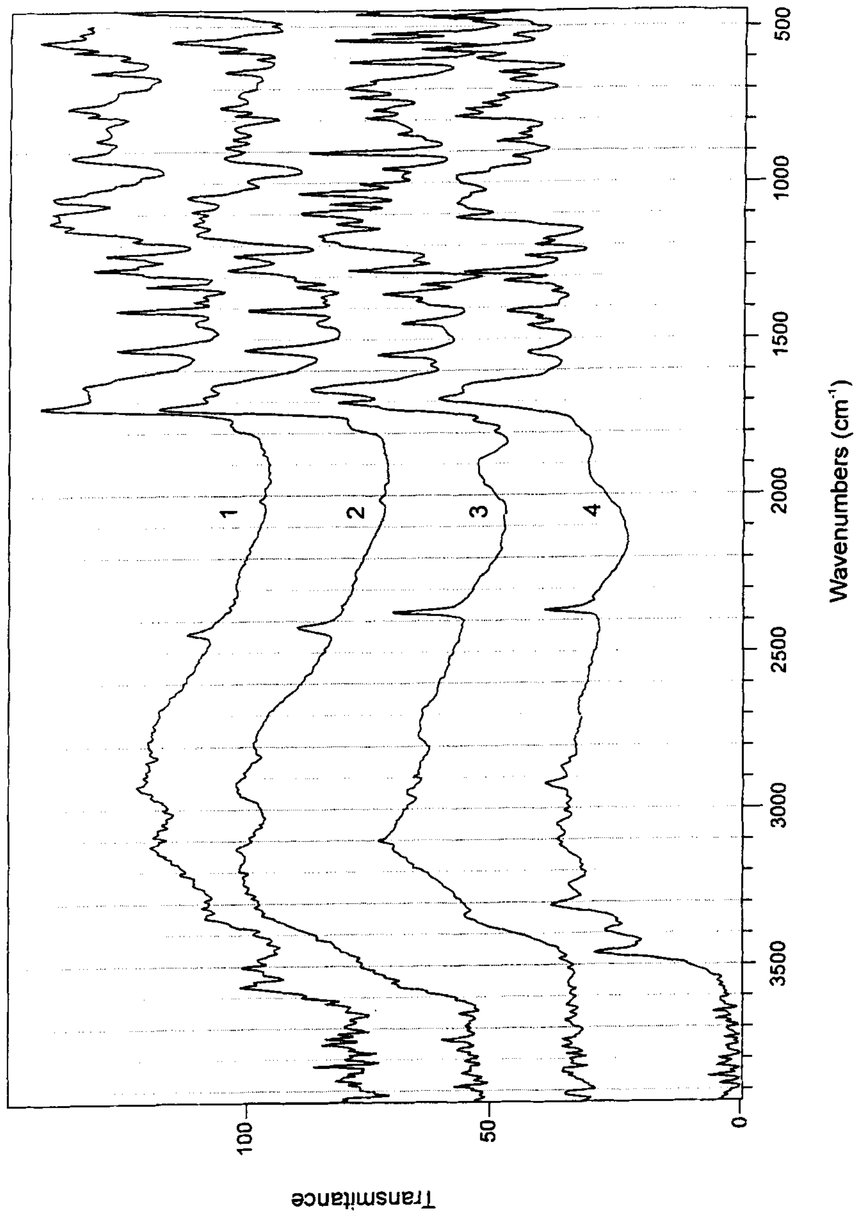

Figure 2. FTIR-PAS spectra of cytidinium H-phosphonate monohydrate (1), cytidinium H-phosphonate (2), bis 2'-deoxy-cytidinium H-phosphonate (3) and 2'-deoxycytidinium H-phosphonate (4).

TABLE 2. Selected bond lengths [Å] and angles [°] for:
(a) $CydH^{+}{\cdot}H_2PO_3^{-}{\cdot}H_2O$, (b) $(dCydH^{+})_2{\cdot}HPO_3^{2-}$ and (c) $dCydH^{+}{\cdot}H_2PO_3^{-}$.

(a) $CydH^{+}{\cdot}H_2PO_3^{-}{\cdot}H_2O$

O(1)-C(2)	1.207(4)
O(4')-C(1')	1.402(3)
O(4')-C(4')	1.464(3)
O(2')-C(2')	1.411(4)
O(3')-C(3')	1.424(4)
O(5')-C(5')	1.399(4)
O(1W)-H(1W)	1.00(6)
O(1W)-H(2W)	0.78(5)
N(1)-C(6)	1.352(4)
N(1)-C(2)	1.377(4)
N(1)-C(1')	1.481(3)
N(3)-C(4)	1.349(4)
N(3)-C(2)	1.383(4)
N(3)-H(3)	0.91(6)
N(4)-C(4)	1.308(4)
C(4)-C(5)	1.398(4)
C(5)-C(6)	1.355(4)
C(1')-C(2')	1.525(4)
C(2')-C(3')	1.528(4)
C(3')-C(4')	1.524(4)
C(4')-C(5')	1.502(5)
P(1)-O(3P)	1.490(2)
P(1)-O(2P)	1.490(2)
P(1)-O(1P)	1.565(3)
P(1)-H(1P)	1.29(3)
O(1P)-H(2P)	0.75(2)

C(1')-O(4')-C(4')	110.1(2)
H(1W)-O(1W)-H(2W)	104(5)

C(6)-N(1)-C(2)	121.9(2)
C(6)-N(1)-C(1')	120.3(2)
C(2)-N(1)-C(1')	117.7(2)
C(4)-N(3)-C(2)	124.7(3)
O(1)-C(2)-N(1)	123.5(3)
O(1)-C(2)-N(3)	121.3(3)
N(1)-C(2)-N(3)	115.1(3)
N(4)-C(4)-N(3)	119.1(3)
N(4)-C(4)-C(5)	123.1(3)
N(3)-C(4)-C(5)	117.7(3)
C(6)-C(5)-C(4)	118.9(3)
N(1)-C(6)-C(5)	121.6(3)
O(4')-C(1')-N(1)	108.2(2)
O(4')-C(1')-C(2')	105.7(2)
N(1)-C(1')-C(2')	112.4(2)
O(2')-C(2')-C(1')	111.2(2)
O(2')-C(2')-C(3')	114.5(2)
C(1')-C(2')-C(3')	100.9(2)
O(3')-C(3')-C(4')	108.9(2)
O(3')-C(3')-C(2')	110.5(2)
C(4')-C(3')-C(2')	102.5(2)
O(4')-C(4')-C(5')	110.0(3)
O(4')-C(4')-C(3')	105.3(2)
C(5')-C(4')-C(3')	114.8(3)
O(5')-C(5')-C(4')	109.7(3)
O(3P)-P(1)-O(2P)	114.45(13)
O(3P)-P(1)-O(1P)	113.2(2)
O(2P)-P(1)-O(1P)	105.8(2)

(b) $(dCydH^{+})_2{\cdot}HPO_3^{2-}$

O(11)-C(21)	1.231(3)
O(3'1)-C(3'1)	1.418(3)
O(4'1)-C(1'1)	1.402(3)
O(4'1)-C(4'1)	1.440(3)
O(5'1)-C(5'1)	1.422(4)
N(31)-C(41)	1.351(3)
N(31)-C(21)	1.367(3)
N(31)-H(31)	0.97(4)
N(11)-C(61)	1.359(3)
N(11)-C(21)	1.383(3)
N(11)-C(1'1)	1.496(3)
N(41)-C(41)	1.313(3)
C(41)-C(51)	1.414(4)
C(51)-C(61)	1.336(4)
C(1'1)-C(2'1)	1.515(4)
C(2'1)-C(3'1)	1.519(4)
C(3'1)-C(4'1)	1.521(4)
C(4'1)-C(5'1)	1.508(4)

O(12)-C(22)	1.219(3)
O(3'2)-C(3'2)	1.426(3)
O(4'2)-C(1'2)	1.418(3)
O(4'2)-C(4'2)	1.454(3)
O(5'2)-C(5'2)	1.412(4)
N(12)-C(62)	1.362(3)
N(12)-C(22)	1.382(3)
N(12)-C(1'2)	1.479(3)
N(32)-C(42)	1.356(3)
N(32)-C(22)	1.379(3)
N(42)-C(42)	1.312(3)
C(42)-C(52)	1.412(4)
C(52)-C(62)	1.335(4)
C(1'2)-C(2'2)	1.509(3)
C(2'2)-C(3'2)	1.513(3)
C(3'2)-C(4'2)	1.524(3)
C(4'2)-C(5'2)	1.510(4)
P(1)-O(2P)	1.517(2)
P(1)-O(3P)	1.517(2)
P(1)-O(1P)	1.524(2)
P(1)-H(1P)	1.32(2)

TABLE 2 Continued

C(1'1)-O(4'1)-C(4'1)	111.5(2)
C(41)-N(31)-C(21)	124.6(2)
C(61)-N(11)-C(21)	120.5(2)
C(61)-N(11)-C(1'1)	122.3(2)
C(21)-N(11)-C(1'1)	117.1(2)
O(11)-C(21)-N(31)	122.2(2)
O(11)-C(21)-N(11)	121.8(2)
N(31)-C(21)-N(11)	116.0(2)
N(41)-C(41)-N(31)	119.9(2)
N(41)-C(41)-C(51)	122.7(3)
N(31)-C(41)-C(51)	117.4(2)
C(61)-C(51)-C(41)	118.6(3)
C(51)-C(61)-N(11)	122.6(2)
O(4'1)-C(1'1)-N(11)	107.5(2)
O(4'1)-C(1'1)-C(2'1)	107.3(2)
N(11)-C(1'1)-C(2'1)	114.1(2)
C(1'1)-C(2'1)-C(3'1)	105.3(2)
O(3'1)-C(3'1)-C(2'1)	113.3(2)
O(3'1)-C(3'1)-C(4'1)	107.6(2)
C(2'1)-C(3'1)-C(4'1)	103.2(2)
O(4'1)-C(4'1)-C(5'1)	109.0(2)
O(4'1)-C(4'1)-C(3'1)	106.3(2)
C(5'1)-C(4'1)-C(3'1)	116.3(2)
O(5'1)-C(5'1)-C(4'1)	111.7(2)
C(1'2)-O(4'2)-C(4'2)	109.6(2)
C(62)-N(12)-C(22)	121.5(2)
C(62)-N(12)-C(1'2)	119.7(2)

(c) dCydH$^+$·H$_2$PO$_3^-$

O(4')-C(1')	1.412(3)
O(4')-C(4')	1.443(3)
O(3')-C(3')	1.404(3)
N(3)-C(4)	1.344(4)
N(3)-C(2)	1.381(4)
O(5')-C(5')	1.424(4)
C(1')-N(1)	1.499(4)
C(1')-C(2')	1.513(4)
O(1)-C(2)	1.208(4)
C(3')-C(2')	1.517(4)
C(3')-C(4')	1.526(4)
C(4)-N(4)	1.316(4)
C(4)-C(5)	1.423(4)
N(1)-C(6)	1.353(4)
N(1)-C(2)	1.387(3)
C(5')-C(4')	1.502(4)
C(5)-C(6)	1.345(4)
P(1)-O(2P)	1.477(2)
P(1)-O(1P)	1.492(3)
P(1)-O(3P)	1.552(3)
P(1)-H(1P)	1.34(4)

C(1')-O(4')-C(4')	110.1(2)
C(4)-N(3)-C(2)	125.0(2)

C(22)-N(12)-C(1'2)	118.7(2)
C(42)-N(32)-C(22)	124.1(2)
O(12)-C(22)-N(32)	121.1(2)
O(12)-C(22)-N(12)	123.4(2)
N(32)-C(22)-N(12)	115.5(2)
N(42)-C(42)-N(32)	118.6(2)
N(42)-C(42)-C(52)	123.4(2)
N(32)-C(42)-C(52)	118.0(2)
C(62)-C(52)-C(42)	118.7(2)
C(52)-C(62)-N(12)	122.1(2)
O(4'2)-C(1'2)-N(12)	107.6(2)
O(4'2)-C(1'2)-C(2'2)	106.5(2)
N(12)-C(1'2)-C(2'2)	113.3(2)
C(1'2)-C(2'2)-C(3'2)	102.6(2)
O(3'2)-C(3'2)-C(2'2)	111.8(2)
O(3'2)-C(3'2)-C(4'2)	107.6(2)
C(2'2)-C(3'2)-C(4'2)	103.1(2)
O(4'2)-C(4'2)-C(5'2)	109.0(2)
O(4'2)-C(4'2)-C(3'2)	106.1(2)
C(5'2)-C(4'2)-C(3'2)	115.5(2)
O(5'2)-C(5'2)-C(4'2)	110.2(2)
O(2P)-P(1)-O(3P)	112.60(10)
O(2P)-P(1)-O(1P)	113.17(10)
O(3P)-P(1)-O(1P)	111.15(10)
O(2P)-P(1)-H(1P)	105.4(11)
O(3P)-P(1)-H(1P)	107.1(11)
O(1P)-P(1)-H(1P)	106.8(10)

O(4')-C(1')-N(1)	108.5(2)
O(4')-C(1')-C(2')	106.6(2)
N(1)-C(1')-C(2')	111.3(2)
O(3')-C(3')-C(2')	113.6(2)
O(3')-C(3')-C(4')	113.8(2)
C(2')-C(3')-C(4')	100.9(2)
N(4)-C(4)-N(3)	119.6(3)
N(4)-C(4)-C(5)	122.5(3)
N(3)-C(4)-C(5)	117.9(3)
C(6)-N(1)-C(2)	121.4(2)
C(6)-N(1)-C(1')	122.4(2)
C(2)-N(1)-C(1')	116.2(2)
C(1')-C(2')-C(3')	101.8(2)
O(5')-C(5')-C(4')	111.2(2)
C(6)-C(5)-C(4)	117.6(3)
C(5)-C(6)-N(1)	122.9(2)
O(1)-C(2)-N(3)	122.1(2)
O(1)-C(2)-N(1)	122.9(3)
N(3)-C(2)-N(1)	115.0(3)
O(4')-C(4')-C(5')	110.1(2)
O(4')-C(4')-C(3')	104.1(2)
C(5')-C(4')-C(3')	116.3(2)
O(2P)-P(1)-O(1P)	116.5(2)
O(2P)-P(1)-O(3P)	111.0(2)
O(1P)-P(1)-O(3P)	110.5(2)

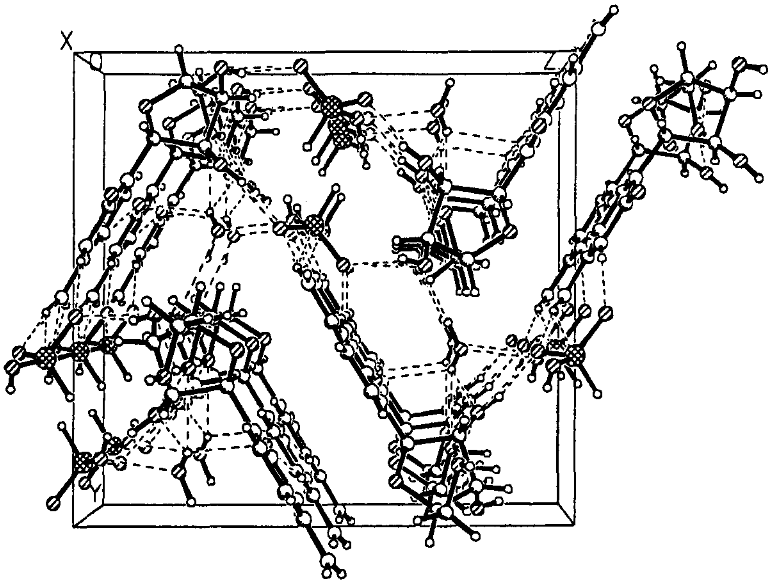

Figure 3. 3D-packing of cytidinium H-phosphonate monohydrate molecules - view along X axis - illustration of H-bond network.

time being an acceptor of H4' and H2P atoms from 1-x, 1/2+y, -1/2-z related molecules. The anions in this structure form pairs of $H_2PO_3^-$ rows with water molecules close to the anions located in a parallel manner to the X direction in the crystal lattice.

The reference data describing the geometry of these hydrogen bonds are shown in Table 3. An illustration of the hydrogen bonding network is shown in Figs 3-5. In fact, the crystal structures of all three compounds are built up from pleated sheets consisting of columns of stacked cations and anions. Additionally, the cations form dimeric pairs in an antyparallel manner due to strong dipol-dipol interactions and other types of weak interactions. The molecular planes - slightly shifted - are overlayed forming 3D structure.

Two positively charged $dCydH^+$ fragments taken from $(dCydH^+)_2{\cdot}HPO_3^{2-}$ fragments form a pair of nucleosides via H-bond interactions with the anion. The residues are arranged in a long chain of molecules parallel to the X axis (Fig. 4a). This plot also indicates that the pleated sheets formed are joined by H-bonding with the neighbouring sheets. Fig. 4b illustrates nice organisation of the $dCydH^+$ cations around the rows of the anions. There are three different groups of H-bonds in this structure due to: (a) OH groups of the sugar parts (O31', O32', O51' and O52') H-bonded to the two oxygen atoms of the anion (O3P and O1P [x,1+y,1+z])

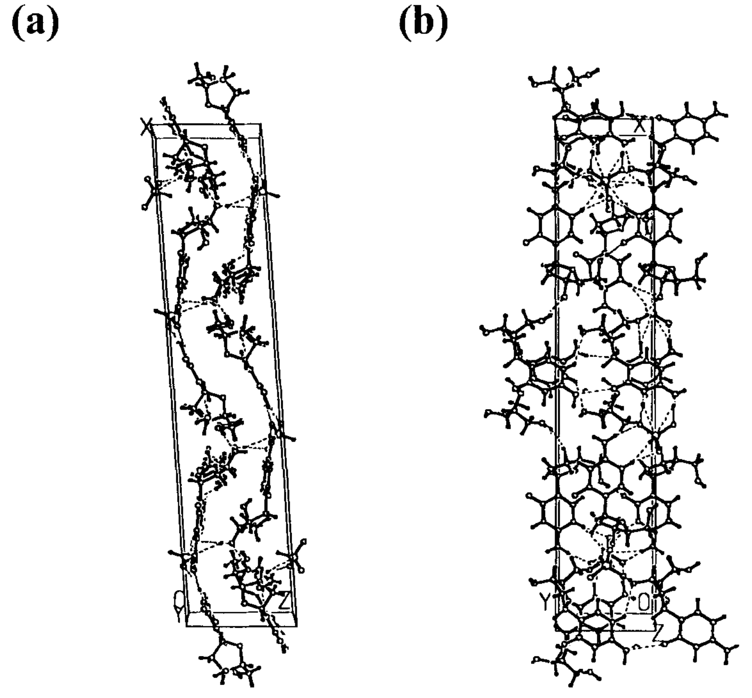

Figure 4. 3D-packing of bis 2'-deoxycytidinium H-phosphonate molecules - view along Y (a) and Z (b) axis.

and to O11 [x,-1+y,z] and O31' oxygens, (b) the N-H donor groups (N31, N32, N41 and N42 atoms) involved in H-bonds mostly to the anion oxygens (O1P, O2P, O3P and O12 from the molecules related by 1/2-x, 1/2+y, 1-z; -x,y,1-z; 1/2-x, ±1/2+y, 1-z; -x, y, 1-z and x, y-1, z symmetry), (c) finally four C-H interactions (C51, C52, C61 and C62) with O3P [1/2-x, -1/2+y,1-z] from the anion and two O-H groups (O32' [x,y-1,z], O51' and O52') from the sugar part. There is also a number of short contacts between the N-H groups and P atoms.

The structure of dCydH$^+$•H$_2$PO$_3^-$ (Fig. 1c) consists of two residues: protonated cation and the H-phosphonate anion. It has a strong ionic character. The moieties are packed in stacks which is well illustrated in a projection along the X-axis (Fig. 5). Each dCydH$^+$ residue is surrounded in YZ plane by four H$_2$PO$_3^-$ anions linked by different types of hydrogen bonding (Table 3). In three of the H-bonds protons are donated by N-H groups (N3 and N4 atoms) from a given dCydH$^+$ moiety. The hydrogens are accepted by O2P [1+x, y,z], O1P [1-x, -3/2+y, 1-z] and O2P [1+x, y, z]. The other three H-bonds are formed by OH groups (one from the phosphonate anion and two from the sugar part: O3' and O5'] with another oxygens as

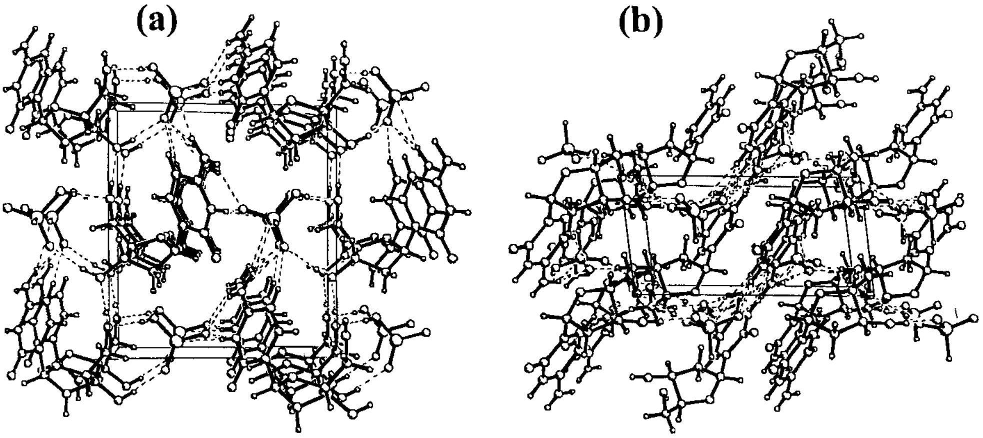

Figure 5. 3D-packing of molecules 2'-deoxycytidinium H-phosphonate - view along X (a) and Y(b) axis illustrating the H-bond network.

acceptors: O5' [x,y,1+z], O1P [x,y,z-1] and O3' [-x, y-1/2, -z]. There are also weak C-H...O H-bonds with C5 and C6 carbons as donors and O1P [1-x, -3/2+y, 1-z] and O5' atoms as acceptors.

The cytosine fragment directly interacts only with the anions whereas the sugar part forms hydrogen bonds to $H_2PO_3^-$ anions as well as to two sugar fragments from another molecules the closest in the crystal lattice. All these H-bonds form quite complicated 2D pattern in YZ plane (Fig. 4). However, it is also obvious from the XZ projection that the $H_2PO_3^-$ anions join parallel molecular sheets of $dCydH^+$ moieties forming, in fact, 3D H-bonded network. This kind of the 3D H-bonding pattern is quite different from the one in the phosphate salts[2,3]. The hemi- salt $(dCyd)_2H^+{\cdot}H_2PO_4^-$ contains two independent $dCydH^+$...dCyd cationic nucleoside pairs composed of protonated and neutral nucleoside with $N(3)^+$-H...N(3) hydrogen bond[3]. The $(dCyd)_2H^+{\cdot}H_2PO_4^-$ structure contains columns of H-bonded dihydrogenphosphate anions. Also in the $dCydH^+H_2PO_3^-$ structure some columns of anions are formed by $H_2PO_3^-$ residues although the anion moieties are not linked by hydrogen bonding (Fig. 6). The shortest P...P distance in the column is equal to 5.329 Å. The P-H hydrogen atom is located along the P...P line with P-H bond length equal to 1.34 Å and H...P contact equal to 4.01 Å.

Similar type of crystal lattice can be found in Cyd and dCyd sulfates and halides[4]. The P-OH distance in the H-phosphonate anions (1.565 Å in $Cyd{\cdot}H_3PO_3{\cdot}H_2O$ and 1.552 Å in $dCydH^+{\cdot}H_2PO_3$) is significantly longer than the other PO bonds (equal on average 1.49 Å for

TABLE 3. Analysis of Potential Hydrogen Bonds in all three cytidine salts.

Nu	Donor-H...Acceptor D-H...A	[Symmetry]	D-H [Å]	H.A [Å]	D.A [Å]	D-H.A [°]
	(a) $CydH^+ \cdot H_2PO_3^- \cdot H_2O$					
1	O(2')-H(2'O)..O(3P)	[-1/2+x,1/2-y,1-z]	0.86	1.82	2.667	167
2	N(3)-H(3)..O(2)	[1-x,1/2+y,1/2-z]	0.91	1.92	2.759	154
3	O(3')-H(3')..O(2P)	[x,y,z]	0.74	1.96	2.678	164
4	O(5')-H(4'O)..O(2')	[-1+x,y,z]	0.93	2.06	2.890	148
5	O(5')-H(4'O)..O(3')	[-1+x,y,z]	0.93	2.48	3.236	138
6	O(1W)-H(1W)..O(3')	[1-x,1/2+y,1/2-z]	1.00	1.92	2.753	138
7	O(1W)-H(2W)..O(1)	[x,y,z]	0.78	2.56	3.116	129
8	O(1W)-H(2W)..O(2')	[x,y,z]	0.78	2.40	3.011	136
9	O(1W)-H(2W)..O(5')	[1+x,y,z]	0.78	2.45	2.977	126
10	N(4)-H(31)..O(1P)	[-x,1/2+y,1/2-z]	0.81	2.24	2.910	140
11	N(4)-H(32)..P(1)	[1-x,1/2+y,1/2-z]	0.88	2.84	3.610	147
12	N(4)-H(32)..O(3P)	[1-x,1/2+y,1/2-z]	0.88	1.89	2.756	171
13	C(5)-H(5)..O(1)	[-1+x,y,z]	0.83	2.51	3.098	129
	(b) $(dCydH^+)_2 \cdot HPO_3^{2-}$					
1	O(52')-H(4O2)..O(31')	[x,y,z]	0.92	1.95	2.838	161
2	O(32')-H(3O2)..O(1P)	[x,1+y,1+z]	0.90	1.85	2.747	174
3	O(31')-H(3O1)..O(3P)	[x,y,z]	0.79	1.91	2.694	176
4	O(51')-H(4O1)..O(11)	[x,-1+y,z]	0.85	1.99	2.835	174
5	N(31)-H(31)..P(1)	[1/2-x,1/2+y,1-z]	0.97	2.78	3.702	159
6	N(31)-H(31)..O(3P)	[1/2-x,1/2+y,1-z]	0.97	1.65	2.604	167
7	N(32)-H(32)..P(1)	[-x,y,1-z]	1.02	2.75	3.697	154
8	N(32)-H(32)..O(2P)	[-x,y,1-z]	1.02	1.63	2.648	177
9	N(41)-H(411)..P(1)	[1/2-x,1/2+y,1-z]	0.92	2.87	3.736	156
10	N(41)-H(411)..O(1P)	[1/2-x,1/2+y,1-z]	0.92	1.97	2.878	167
11	N(41)-H(412)..O(2P)	[1/2-x,-1/2+y,1-z]	0.94	2.05	2.972	165
12	N(42)-H(421)..P(1)	[-x,y,1-z]	0.99	2.71	3.637	157
13	N(42)-H(421)..O(1P)	[-x,y,1-z]	0.99	1.75	2.732	170
14	N(42)-H(422)..O(12)	[x,-1+y,z]	0.81	2.14	2.905	156
15	C(51)-H(51)..O(3P)	[1/2-x,-1/2+y,1-z]	0.86	2.26	3.128	171
16	C(52)-H(52)..O(32')	[x,-1+y,z]	0.95	2.56	3.251	130
17	C(61)-H(61)..O(51')	[x,y,z]	0.93	2.42	3.290	156
18	C(62)-H(62)..O(52')	[x,y,z]	0.99	2.34	3.284	161
	(c) $dCydH^+ \cdot H_2PO_3^-$					
1	O(3P)-H(2P)..O(5')	[x,y,1+z]	0.72	1.91	2.627	174
2	N(3)--H(3)..P(1)	[1+x,y,z]	0.92	2.88	3.797	175
3	N(3)--H(3)..O(2P)	[1+x,y,z]	0.92	1.73	2.615	160
4	O(3')-H(3O)..O(1P)	[x,y,-1+z]	0.83	1.80	2.630	172
5	N(4)-H(4A)..O(1P)	[1-z,-3/2+y,1-z]	1.02	1.93	2.903	159
6	N(4)-H(4B)..O(2P)	[1+x,y,z]	0.80	2.28	2.968	144
7	O(5')-H(5'A)..O(3')	[-x,-1/2+y,-z]	0.78	1.86	2.647	176
8	C(5)-H(5A)..O(1P)	[1-z,-3/2+y,1-z]	0.92	2.52	3.247	137
9	C(6)-H(6)..O(5')	[x,y,z]	0.99	2.26	3.208	159

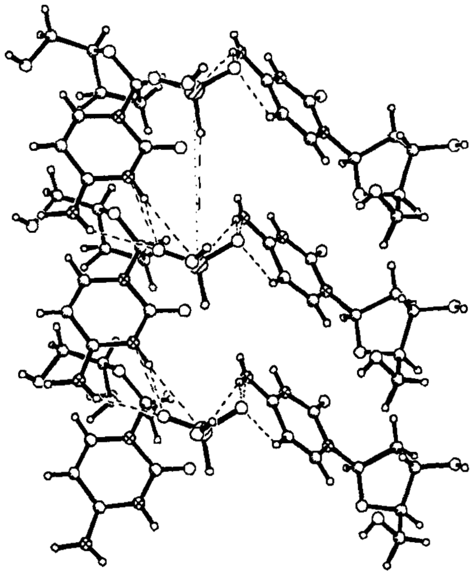

Figure 6. Ordering of organic moieties around $H_2PO_3^-$ row.

the hydrate and 1.48 Å for the other compound). This is mainly due to the fact that the other PO bonds have a double character - in contrast to the singular P-OH bond. The PO bond lengths in the phosphonates are, in fact, quite similar to the bonds in phosphate anions[2]. Some small differences in their lengths can be attributed to different hydrogen bonds formed in these two classes of salts.

There is an interesting situation in the bis 2'-deoxycytidinium H-phosphonate $[(dCydH^+)_2{\cdot}HPO_3^{2-}]$, where all three PO bonds have almost equal bond lengths (ca. 1.52 Å). This equalization of P=O and P-O bonds in the HPO_3^{2-} anion results from proton transfer of acidic POH hydrogens to the base residues (protonation of N3 atoms). Most of phosphonate oxygen atoms are involved in hydrogen bonding.

The glycosidic torsion angle χ [C2N1C1'O4'], describing the relative orientation of the base with respect to the sugar, is in the range from 133° up to 164° for all studied compounds (Table 4) and indicates the anti (-ac) conformation about the glycosyl bond. The conformation of the ribose ring is close to 2'-endo ^2E for $CydH^+{\cdot}H_2PO_3^-{\cdot}H_2O$ and the second molecular fragment $dCydH^+$ of $(dCydH^+)_2{\cdot}HPO_3^{2-}$. For the first $dCydH^+$ moiety it is close to ^3E whereas for the third compound, $dCydH^+{\cdot}H_2PO_3^-$, it is in-between ^3E and $^3T_2$. The values of parameters describing the conformation of the ribose ring in terms of pseudorotation are given in Table 4.

TABLE 4. Description of conformation and puckering parameters.

Parameter	**$CydH^+ \cdot H_2PO_3^- \cdot H_2O$**	**$(dCydH^+)_2 \cdot HPO_3^{2-}$**		**$dCydH^+ \cdot H_2PO_3^-$**
Orientation about glycosyl bond	anti (-ac)	anti (-ac)	Anti (-ac)	anti (-ac)
Glicosyl torsion angle χ C2N1C1'O4' [°]	-145.1	-164.2	-133.1	-164.3
Symbol of ribose pucker	^2E C2'-endo	^3E C3'1-endo	^2E C2'2-endo	$^3E/^3T_2$ C3'-endo
Pseudorotation phase angle P [°]*	165.9	16.8	167.0	9.1
Degree of pucker τ_m.*	39.7	25.8	35.1	40.6
Conformation of the side chain	+sc	+sc	+sc	+sc
Torsion angle γ O5'C5'C4'C3'	51	55	54	50
Cremer&Pople's Q(2) [Å]**	0.386	0.249	0.338	0.398
Cremer&Pople's Φ_2 [Å]**	221.5	69.7	222.5	62.9

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The side chain (C5'O5') exists in all these salts in +sc conformation (see the values of γ angle = O5'C5'C4'C3' in Table 4 - all close to 50°).

We conclude that all three salts of H_3PO_3 have similar geometry and conformation but they significantly differ as far as their H-bonding networks are concerned. Contrary to the phosphates of cytidine and deoxycytidine, the phosphonates do not form direct base pairs but they strongly interacts with the $H_2PO_3^-$ and HPO_3^{-2} anions present in the crystal lattice. This seems to be more favourable than the base-base interactions. All three salts form a complex 3D H-bond networks which hardly differentiates the bond lengths in the nucleosides. As a result pleated sheets are formed consisting from alternating columns of the cations and anions. The sheets are joined by additional O-H...O=P bonds thus giving 3D networks.

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