Preparation and X-Ray Study of Inclusion Complexes of (4Z,5E)-Pyrimidine-2,4,5,6(1H,3H)-Tetraone 4,5-Dioxime and the Product of Its Cyclization, (1,2,5)-Oxadiazolo(3,4-d)-Pyrimidine-5,7(4H,6H)-Dione with Two 18-Membered Macrocycles *

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Abstract

The novel dioxime, (4Z,5E)-pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime (H_2-PTD) was obtained by the interaction of 6-amino-5-nitrosopyrimidine-2,4(1H,3H)-dione with hydroxylamine hydrochloride. X-ray structural analysis determined the 4Z,5E-configuration of the corresponding monoanion, pyrimidine-2,6(1H,3H)-dione-4-iminole-5-iminolate in the inclusion complexes with diazonia-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane) (H_2-DA18C6)$^{2+}$ (complex (**1**), stoichiometry 2 : 1), and its ammonium salt in the complex with the *cis-syn-cis* isomer of dicyclohexano-18-crown-6(DCHA) (*cis-syn-cis*-2,5,8,15,18,21-hexaoxatricyclo(20.4.0.0^{9,14})hexacosane) (complex (**2**), stoichiometry 1 : 1). X-ray data were also obtained for the complex of the product of (H_2-PTD) cyclization, (1,2,5)-oxadiazolo(3,4-d)pyrimidine-5,7(4H,6H)-dione (OPD) with diaqua diaza-18-crown-6 (complex (**3**), stoichiometry 2 : 2 : 1).

In (**1**) the (H-PTD)$^-$ anions are joined into dimers through the bifurcated OH···N and OH···O hydrogen bonds and alternate with diazonia-18-crown-6 cations in the chains sustained by the NH(crown)···O and NH(crown)···N interactions. The chains are further combined into the 3D network *via* NH···O(crown) hydrogen bonds. In (**2**) the self-complementarity of the (H-PTD)$^-$ anions facilitates their assembly into the chain *via* OH···N, NH···O and OH···O interactions. The ammonium cations bridge each anion and the DCHA macrocycle with the formation of a ribbon developed along the [101] direction in the unit cell. Ternary complex (**3**) is built of the neutral species, diaza-18-crown-6, water molecules and dimers of OPD alternated in the chains and held together by OH···O and NH···O hydrogen bonds.

Introduction

Crown ethers and related macrocycles deserve the considerable attention for their host–guest chemistry as receptors for cations and neutral organic molecules [1]. These double-face spacers are capable to be included in the extended supramolecular networks formulated by the self-assembled neutral organic molecules, rich in both H-donor and acceptor centers with the final partial retention or rearrangement of H-bonds which sustain the supramolecular architecture [2].

We intended to prepare the novel dioxime, pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime (H_2-PTD) and study its ability to complex with 18-membered crown ethers.

Another task was to elucidate in which of four possible tautomeric forms the (H_2-PTD) molecule is present in the crown ether complexes and what factors are decisive for the stabilization of the preferable tautomer.

The most widely used way of the preparation of pyrimidines containing exocyclic functional groups includes the attack of the corresponding nucleophiles on the chloropyrimidines [3, 4]. Essentially less attention has been devoted to the reactions of overamination [5, 6], notwithstanding that in several cases the aminopyrimidines are more accessible than the corresponding chloropyrimidines [3, 4].

It is known that 6-amine-5-nitrosopyrimidine-2,4-(1H,3H)-dione (**I**) easily participates in the acid catalysed metathesis reaction of the amine group by hydroxylamine.

The product of the reaction, 6-(hydroxyamino)-5-nitrosopyrimidine-2,4(1H,3H)-dione (**II**) may also exist in three other tautomeric forms, (**III–V**), 6-
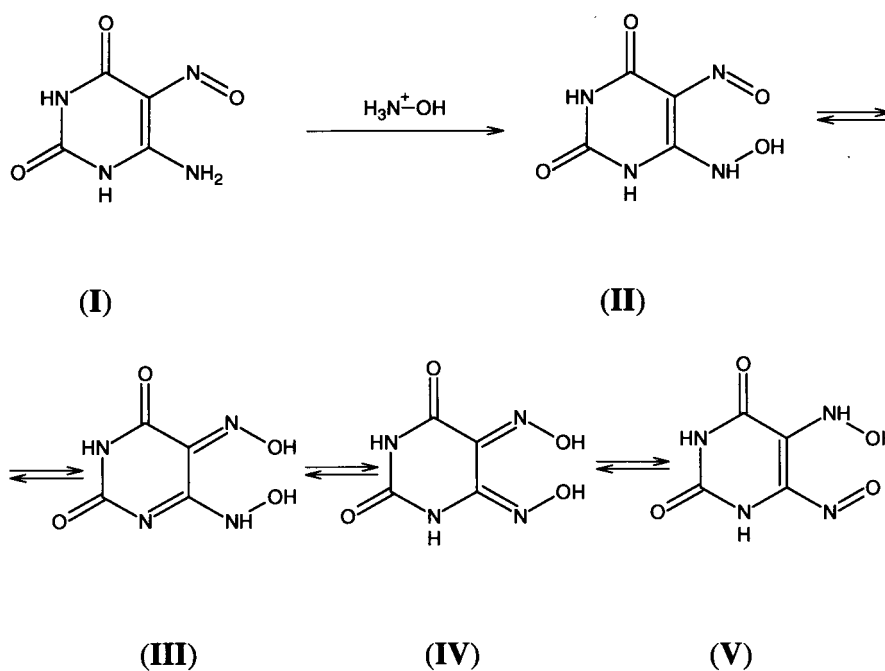
Scheme **I–V**.

(hydroxyamino) pyrimidine-2,4,5(3H)-trione-5-oxime, (III), pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime, (IV), 5-(hydroxyamino)-6-nitrosopyrimidine-2,4(1H,3H)-dione, (V). The absence of the color, that is the specific feature of the nitrosouracils, permits us with high probability to exclude the presence of tautomers (II) and (V). In its turn, the tautomer (IV) may exist in the form of one of four stable geometric isomers (IVa–d) or as their mixture.

X-ray data were obtained for the complexes of diazonia-18-crown-6 with (4Z,5E)-isomer of (H-PTD)⁻ anion (1) (1 : 2), its ammonium salt with *cis-syn-cis* isomer of dicyclohexano-18-crown-6 (DCH6A) (2) (1 : 1), and diaza-18-crown-6 and water with (1,2,5)oxadiazolo-(3,4-d)pyrimidine-5,7(4H,6H)-dione, (3) (1 : 2 : 2).

Experimental

Synthesis

The thin layer chromatographic control of the substances purity was performed on the Silufol UV-254 plates. Mass-spectrum was obtained on the Varian MAT-112 instrument using 70 eV ionization radiation, and a temperature of 220 °C. The *IR* spectrum was recorded on a Specord-80 spectrometer of mulls in nujol.

Synthesis of (H₂-PTD)

A mixture of 1.4 g (0.009 mol) of 6-amino-5-nitrosopyrimidine-2,4(1H,3H)-dione (I), 2 g (0.03 mol) of hydroxylamine hydrochloride, 1.6 g (0.02 mol) of sodium acetate in 50 mL of water was heated up to 65–70° and stirred until bleaching the reactive mixture. The precipitate was filtered off, washed by the cold water and air dried. The yield of (H₂-PTD) is 1.4 g (91%). M.P. > 250 °C

with decomposition. Found, C, 27.92, H, 2.36, N, 32.40 for $C_4H_4N_4O_4$. Calculated, %: C, 27.90; H, 2.33; N, 32.56.

IR, v, cm⁻¹: 3320, 3000, 1720, 1680, 1600. Mass-spectrum, m/z (I%): 154(39) − [M⁺-H₂O], 111(12), 70(10), 68(15), 58(8), 54(10), 53(13), 43(100).

Synthesis of (1)

A mixture of 86 mg (0.5 mol) of (H₂-PTD) and 131 mg (0.5 mmol) of diaza-18-crown-6 was dissolved in 5 mL of distilled water and 10 mL of ethanol. The insoluble residue was filtered off and the solvent was allowed to evaporate in ambient conditions. Bright-yellow crystals with the M.P. 175–180 °C with decomposition. Found, C, 39.57, H, 5.69, N, 23.12 for $C_{20}H_{34}N_{10}O_{12}$. Calculated, %: C, 39.60; H, 5.65; N, 23.09.

Synthesis of (2)

86 mg (0.5 mmol) of (H₂-PTD) was dissolved in 5 mL of 25% aqueous ammonia solution, a solution of 186 mg (0.5 mmol) of DCH6A was added and the reactive mixture allowed to evaporate at room temperature. Red monocrystals of the complex were obtained. M.P. 176–177 °C. Found, C, 51.28, H, 7.77, N, 12.51 for $C_{24}H_{43}N_5O_{10}$. Calculated, %: C, 51.31; H, 7.72; N, 12.47.

Synthesis of (3)

(3) was obtained as a minor product in the synthesis of (1) via the cyclisation of (H₂-PTD) in (OPD). The insoluble residue remaining after the separation of complex (1) from the reaction mixture, was mixed with the triple excess of diaza-18-crown-6 and dissolved in the minimal amount of boiling water. Very poor quality colorless crystals were obtained by the recrystallization from water. M.P. 200 °C.

(IVa)   **(IVb)**   **(IVc)**   **(IVd)**
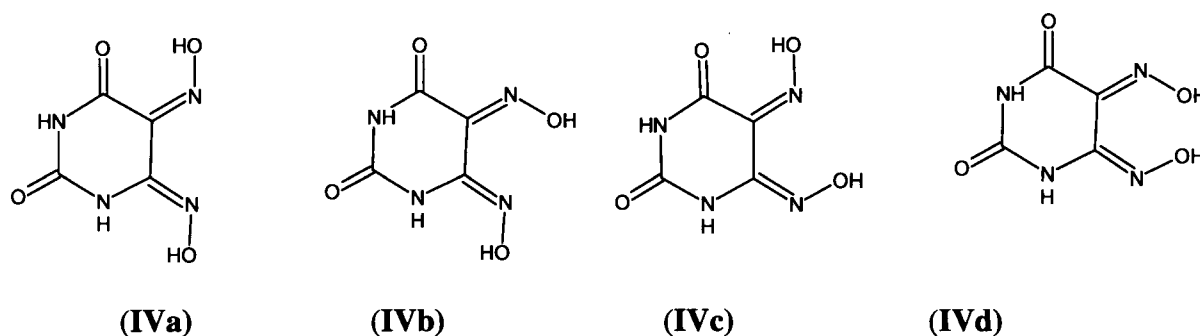
Scheme **IVa–IVd**. **(IVa)** – (4Z,5Z)-pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime
(IVb) – (4Z,5E)-pyrimidine-2,4,5,6(1H,3H)-tetraone-4,5-dioxime
(IVc) – (4E,5Z)-pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime
(IVd) – (4E,5E)-pyrimidine-2,4,5,6(1H,3H)-tetraone 4,5-dioxime

Found, C, 39.62, H, 5.63, N, 23.07 for $C_{20}H_{34}N_{10}O_{12}$. Calculated, %: C, 39.60; H, 5.65; N, 23.09.

Data collection and structure refinement

The X-ray intensity data for (**1**)–(**3**) were collected on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo-Kα radiation using ω rotation with a sample-to-detector distance of 40 mm. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO [7]. The scaling as well as the global refinement of crystal parameters were performed by SCALEPACK [7]. Reflections, which were partly measured on previous and subsequent frames, were used to scale these frames on each other. The structure solution and refinement proceeded similarly for all structures (SHELX-97 software [8]). Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were refined anisotropically (full-matrix least squares method on F^2). C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound H-atoms were found from differential Fourier maps and refined without any constrains.

The X-ray data and the details of the refinement for (**1**)–(**3**) are given in Table 1, the selected geometric parameters are summarized in Table 2.

For (**3**) the intensity data set was obtained for a poor quality twinned crystal. Attempts were made to separate the twinned domains but abandoned, so the refinement was stopped at an *R*-value of 0.1394 and only main features of the supramolecular architecture of (**3**) are further discussed.

Crystallographic data for (**1**)–(**3**) were deposited with the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 180269-180271.

**Results and discussion**

*Structure of the (H-PTD)$^-$ anion in (**1**) and (**2**)*

The molecule of (H$_2$-PTD) present in (**1**) and (**2**) in the form of the monoanion with one oxime group being deprotonated.

The geometric parameters of the uracil heterocycle are very close to the literature data for the relative compounds [9–12]. Due to the conjugation with the *exo*-functional groups all the C—C and C—N interatomic distances are shortened in comparison with the standard values for the corresponding single bonds. All the bond angles at C-atoms approach essentially to 120° (the maximal deviation from this value is 5.1(1)°), while the angles at the N-atom adopt practically the same values in the both complexes equal 126.7(1)° and 126.6(1)°, respectively. The six-membered heterocycle both in (**1**) and (**2**) is practically planar, with the average deviation from complanarity of the six heteroatoms defined the uracil ring being 0.020(1) Å in (**1**) and 0.006(8) Å in (**2**). The deviations of the *exo*-cyclic atoms non-contributing in this plane scatter in the range 0.129(3) for N(4G) to −0.068(3) Å for O(2G) in (**1**) and from 0.079(2) for O(3G) to −0.015(2) Å for N(4G) in (**2**).

*Structure of (**1**)*

The crystal structure of (**1**) is built of the (H-PTD)$^-$ monoanions in general positions and [H$_2$-DA18C6]$^{2+}$ dications which occupy the positions around the inversion centers in the unit cell. The ORTEP diagram [13] of the independent part of the unit cell for (**1**) with the numbering scheme is shown in Figure 1. The components in (**1**) are mutually arranged in such a way, that the dihedral angle between the plane of 6-membered heterocycle of (H-PTD)$^-$ moiety and the plane of the six oxygen atoms of the crown ring is 74.6(1)°. The nitrogen and oxygen atoms of the deprotonated oxime group act as H-acceptors and bridge the symmetry related NH$_2$-groups of the diazonia-18-crown-6 macrocycle, N(4)$\cdots$N(4G) 2.889(2), N(4)$\cdots$O(4G)(−x, −y, −z − 1) 2.742(2) Å. The carbonyl oxygen O(1G) of (H-PTD)$^-$ as H-acceptor also contributes in H-bonding with the crown, N(4)$\cdots$O(1G) 3.009(2) Å, the details of H-bonding geometry for (**1**) and (**2**) are given in Table 3.

Two (H-PTD)$^-$ anions are combined into the centrosymmetric planar dimer *via* the pair of bifurcated OH$\cdots$N and OH$\cdots$O hydrogen bonds with the participation of both oxime groups, protonated (as H-donor) and deprotonated (as H-acceptor) ones, O(3G)$\cdots$N(3G)(−x+1, −y, −z) 2.770(2) Å, R$_2^2$(6) [14], O(3G)$\cdots$O(4G)(−x + 1, −y, −z) 2.810(2)

(1)

(2)

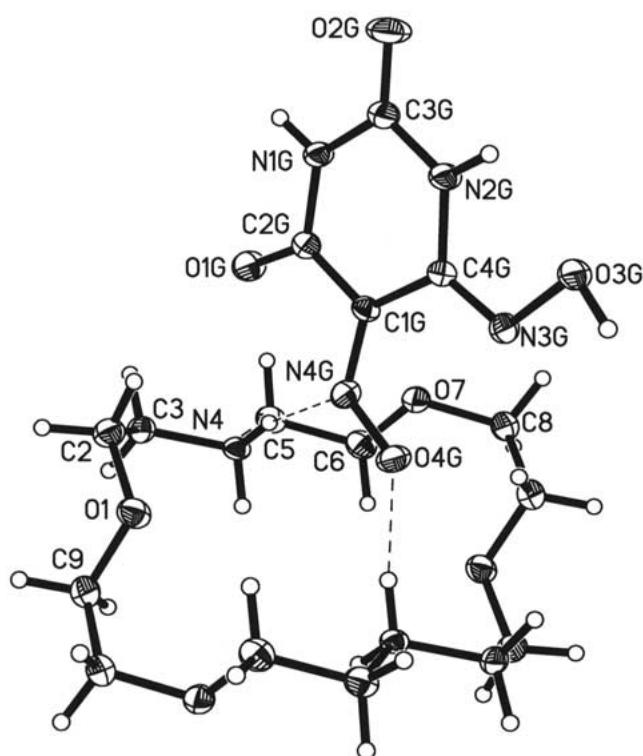
(3)
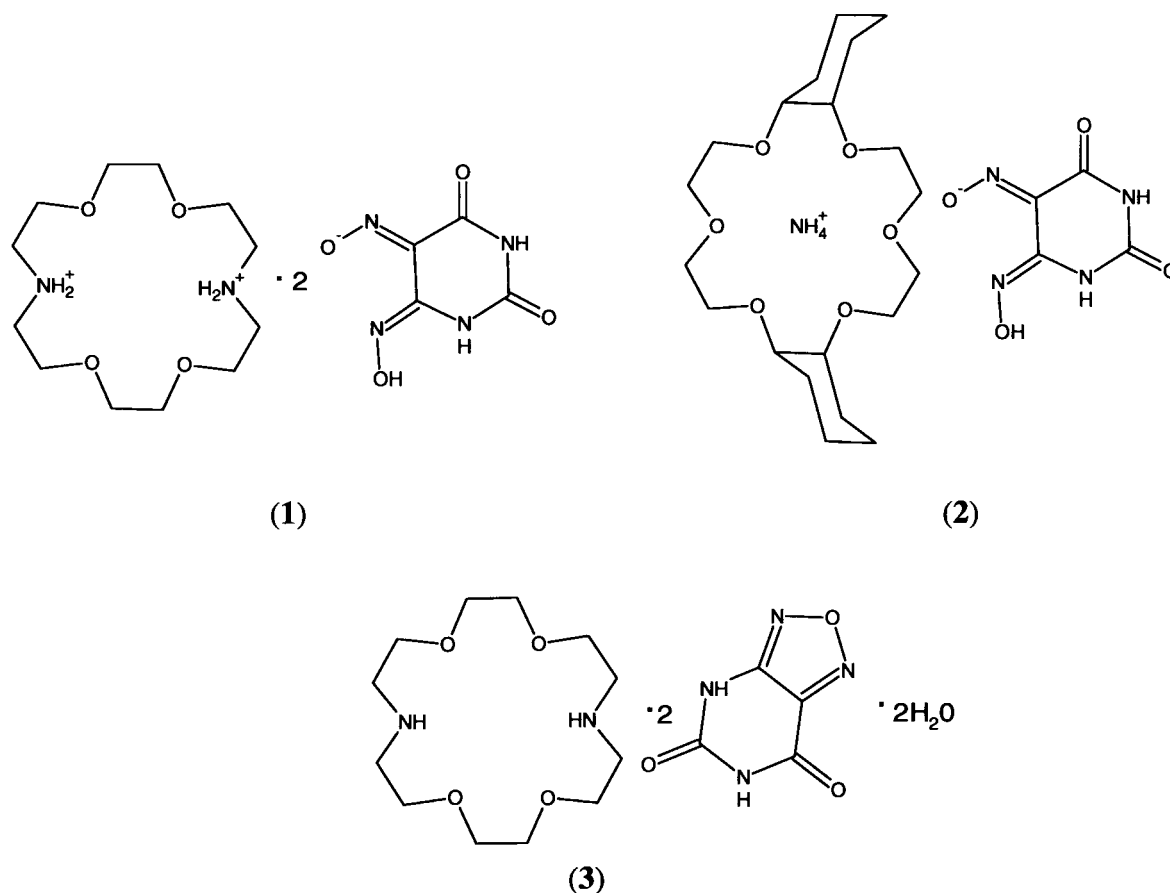
Scheme **1–3**.

Figure 1. ORTEP drawing of (**1**) with atomic numbering scheme and hydrogen bonds shown as dotted lines. Non-hydrogen atoms are represented by thermal ellipsoids at 30% probability. The symmetry related (H-PTD)⁻ anion is omitted for the sake of clarity.
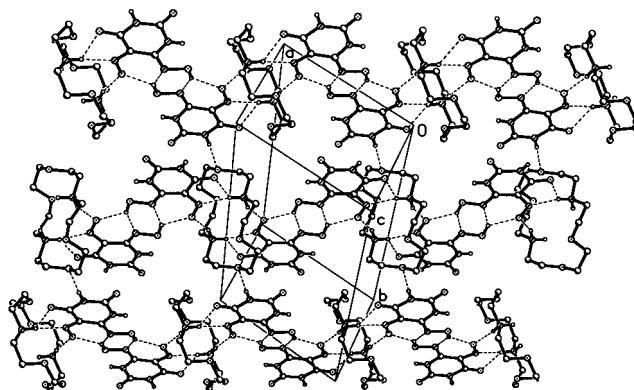

Figure 2. H-bonded chains in (**1**) running along [101] direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

Å R_2^2 (14) graph sets. The [(H-PTD)⁻]₂ dimers alternate with the [H₂-DA18C6]²⁺ cations in the chains running along [101] direction in the unit cell, Figure 2.

Side interactions between the N(1G) atom of the (H-PTDH)⁻ anion and the O(7) oxygen atom of the crown molecule related with the basic one by glide plane, N(1G)···O(7)(x, $-y + 1/2$, $z + 1/2$) 2.881(2) Å are responsible for the joining of these chains in the 3D network, as shown in Figure 3.

Complex (**1**) represents an example of the simple salt of the diazonia-18-crown-6 macrocycle with a bulky organic anion stabilized by H-bonds. Chekhlov et al. [15–17] stud-

Table 1. Crystal data and summary of intensity data collection and structure refinement for compounds (**1**)–(**3**)

| Compound	(**1**)	(**2**)	(**3**)
CCDC number	180269	180270	180271
Empirical formula	$C_{20}H_{34}N_{10}O_{12}$	$C_{24}H_{43}N_5O_{10}$	$C_{20}H_{34}N_{10}O_{12}$
Formula weight	606.58	561.63	608.58
Temperature, K	293(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P-1$	$P-1$
Unit cell dimensions			
a, Å	9.969(3)	10.963(2)	7.178(4)
b, Å	18.673(8)	11.492(2)	7.755(4)
c, Å	7.441(4)	12.236(3)	13.125(1)
α, deg.	–	107.18(1)	74.40(2)
β, deg.	105.72(3)	98.43(1)	78.38(2)
γ, deg.	–	103.06(1)	79.82(3)
Cell volume, Å^3	1333.3(1)	1396.5(5)	683.4(7)
Formula units/unit cell	2	2	1
D_{calc}, g cm^{-3}	1.511	1.336	1.479
μ, mm^{-1}	0.126	0.104	0.123
F(000)	640	604	322
Crystal dimensions, mm	$0.15 \times 0.20 \times 0.25$	$0.20 \times 0.20 \times 0.30$	$0.15 \times 0.25 \times 0.30$
θ range for data collection, deg.	2.39 to 27.49	1.93 to 32.00	2.75 to 27.47
Limiting indices	$-11 < h < 12$,	$0 < h < 16$,	$-9 < h < 9$,
	$-24 < k < 24$,	$-17 < k < 16$,	$-10 < k < 10$,
	$-9 < l < 9$	$-18 < l < 17$	$-16 < l < 16$
Reflections collected/unique	4930/2869	9285/9285	5796/3097
	[R(int) = 0.0305]		[R(int) = 0.1076]
Reflections with $I > 2\sigma(I)$	1906	6776	2167
Refinement method		Full-matrix least-squares on F^2	
Data/restraints/parameters	2869/0/207	9285/0/380	3097/9/203
Goodness-of-fit on F^2	1.029	1.020	1.260
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$,	$R_I = 0.0496$,	$R_1 = 0.1394$,
	$wR_2 = 0.0933$	$wR_2 = 0.1069$	$wR_2 = 0.1695$
R indices (all data)	$R_1 = 0.0857$,	$R_1 = 0.0809$,	$R_1 = 0.2104$
	$wR_2 = 0.1022$	$wR_2 = 0.1167$	$wR_2 = 0.1877$
Largest diff. peak and hole e A^{-3}	0.235 and -0.176	0.313 and -0.260	0.300 and -0.631
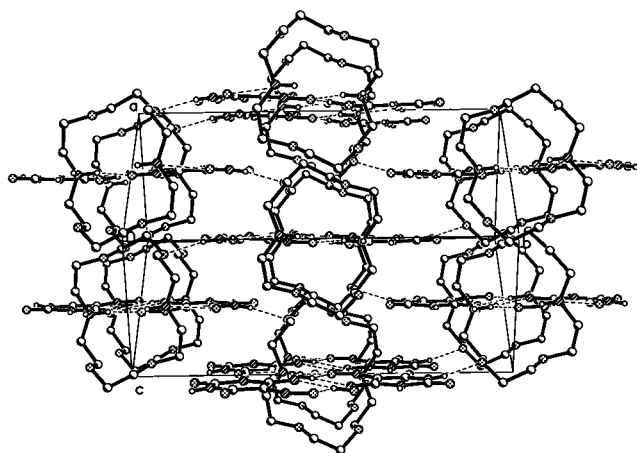
Figure 3. Crystal packing in (**1**). The chains are combined into 3D network along *b* axis *via* NH$\cdots$O(crown) hydrogen bondings.

ied the complexes of diazonia-18-crown-6 of the salt type. He divided them into two main groups, simple salts having the composition [H$_2$DA18C6]$^{2+}\cdot$2An$^-$ with the monoanions, An$^-$: Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, SCN$^-$, CF$_3$CO$_2^-$ etc. [16], and dihydrates of the salts with the composition, [H$_2$DA18C6]$^{2+}\cdot$2An$^-\cdot$2H$_2$O, with the monoanions, An$^-$: HSO$_4^-$, H$_2$PO$_4^-$, HCO$_3^-$, C$_6$H$_5$CO$_2^-$ [17]. The anhydrous complexes are built in such a mode that the anions have short H-bonding contacts with the positively charged NH$_2^+$ centers of the diazonia cations with the formation of 1 : 2 complexes of the 'host–guest type'. Water molecules in the second type of complexes are bound with the anions and formulate the second coordination sphere of a macrocycle and expand the structure in two or three directions. The organization of some complexes is similar to (**1**). Thus, in the 3D structure of the complex of diazonia-18-crown-6 with tartarate tetrahydrate [H$_2$DA18C6]$^{2+}\cdot$C$_4$H$_4$O$_6^{2-}\cdot$4H$_2$O [16c], tartarate dianions, C$_4$H$_4$O$_6^{2-}$ and macrocyclic cations

Table 2. Selected bond distances (Å) and angles (deg) in (**1**)–(**3**)

Geometry of the (H-PTD)⁻ in (**1**) and (**2**)		
	(**1**)	(**2**)
O(1G)—C(2G)	1.223(2)	1.231(1)
O(2G)—C(3G)	1.211(2)	1.220(1)
O(3G)–N(3G)	1.413(2)	1.415(1)
O(4G)—N(4G)	1.289(2)	1.300(1)
C(1G)—N(4G)	1.320(2)	1.331(1)
C(1G)—C(2G)	1.459(2)	1.461(2)
C(1G)—C(4G)	1.461(2)	1.455(1)
C(2G)—N(1G)	1.383(2)	1.391(1)
C(3G)—N(2G)	1.361(2)	1.369(1)
C(3G)—N(1G)	1.372(2)	1.378(2)
C(4G)—N(3G)	1.282(2)	1.296(1)
C(4G)—N(2G)	1.381(2)	1.395(1)
N(4G)—C(1G)—C(2G)	113.9(1)	114.3(1)
N(4G)—C(1G)—C(4G)	127.2(1)	126.8(1)
C(2G)—C(1G)—C(4G)	118.9(1)	118.9(1)
O(1G)—C(2G)—N(1G)	1119.0(2)	118.9(1)
O(1G)—C(2G)—C(1G)	125.1(1)	124.7(1)
N(1G)—C(2G)—C(1G)	115.9(1)	116.3(1)
O(2G)—C(3G)—N(2G)	122.7(2)	122.4(1)
O(2G)—C(3G)—N(1G)	122.2(2)	122.8(1)
N(2G)—C(3G)—N(1G)	115.1(2)	114.9(1)
N(3G)—C(4G)—N(2G)	121.3(1)	120.8(1)
N(3G)—C(4G)—C(1G)	122.3(1)	122.6(1)
N(2G)—C(4G)—C(1G)	116.4(1)	116.7(1)
C(3G)—N(1G)—C(2G)	126.8(2)	126.7(1)
C(3G)—N(2G)—C(4G)	126.7(2)	126.5(1)
C(4G)—N(3G)—O(3G)	110.6(1)	110.1(1)
O(4G)—N(4G)—C(1G)	118.7(1)	117.4(1)

Geometry of the OPD molecule in (**3**)			
O(1G)—C(2G)	1.222(5)	N(4G)—O(3G)—N(3G)	112.1(3)
O(2G)—C(3G)	1.252(5)	C(2G)—N(1G)—C(3G)	128.0(3)
O(3G)—N(4G)	1.377(4)	C(3G)—N(2G)—C(4G)	116.1(4)
O(3G)—N(3G)	1.409(5)	C(4G)—N(3G)—O(3G)	103.9(3)
N(1G)—C(2G)	1.377(5)	C(1G)—N(4G)—O(3G)	104.0(3)
N(1G)—C(3G)	1.410(5)	N(4G)—C(1G)—C(4G)	111.0(4)
N(2G)—C(3G)	1.329(5)	N(4G)—C(1G)—C(2G)	128.4(4)
N(2G)—C(4G)	1.353(5)	C(4G)—C(1G)—C(2G)	120.6(4)
N(3G)—C(4G)	1.320(5)	O(1G)—C(2G)—N(1G)	123.9(4)
N(4G)—C(1G)	1.308(5)	O(1G)—C(2G)—C(1G)	126.7(4)
C(1G)—C(4G)	1.413(6)	N(1G)—C(2G)—C(1G)	109.4(4)
C(1G)—C(2G)	1.470(6)	O(2G)—C(3G)—N(2G)	124.0(4)
		O(2G)—C(3G)—N(1G)	115.1(4)
		N(2G)—C(3G)—N(1G)	120.9(4)
		N(3G)—C(4G)—N(2G)	126.0(4)
		N(3G)—C(4G)—C(1G)	108.9(4)
		N(2G)—C(4G)—C(1G)	125.0(4)

Table 2. Continued

Torsion angles along the heterocyclic framework in (**1**) and (**2**)

	(**1**)		(**2**)
C(9)—O(1)—C(2)—C(3)	−71.7(2)	C(18)—O(1)—C(2)—C(3)	−173.5(1)
O(1)—C(2)—C(3)—N(4)	−50.8(2)	O(1)—C(2)—C(3)—O(4)	−72.0(1)
C(2)—C(3)—N(4)—C(5)	−161.3(1)	C(2)—C(3)—O(4)—C(5)	175.4(1)
C(3)—N(4)—C(5)—C(6)	−175.5(1)	C(3)—O(4)—C(5)—C(6)	176.5(1)
N(4)—C(5)—C(6)—O(7)	−68.0(2)	O(4)—C(5)—C(6)—O(7)	67.4(1)
C(5)—C(6)—O(7)—C(8)	173.4(1)	C(5)—C(6)—O(7)—C(8)	−177.3(1)
C(6)—O(7)—C(8)—C(9)^i	−91.8(2)	C(6)—O(7)—C(8)—C(9)	177.7(1)
O(7)—C(8)—C(9)^i—O(1)^i	65.4(2)	O(7)—C(8)—C(9)—O(10)	−56.3(1)
C(8)—C(9)^i—O(1)^i—C(2)^i	166.3(1)	C(8)—C(9)—O(10)—C(11)	64.5(1)
		C(9)—O(10)—C(11)—C(12)	−168.7(1)
		O(10)—C(11)—C(12)—O(13)	−67.0(1)
		C(11)—C(12)—O(13)—C(14)	171.0(1)
		C(12)—O(13)—C(14)—C(15)	172.9(1)
		O(13)—C(14)—C(15)—O(16)	67.7(1)
		C(14)—C(15)—O(16)—C(17)	176.1(1)
		C(15)—O(16)—C(17)—C(18)	71.3(1)
		O(16)—C(17)—C(18)—O(1)	57.5(1)
		C(17)—C(18)—O(1)—C(2)	−175.0(1)

Symmetry transformations used to generate equivalent atoms: $i - x, -y, -z - 1$.

alternate in the chains, and water molecules combine them into a 3D network. The linear architecture is found in the complex of $[H_2DA18C6]^{2+}$ with the dimers of monoaqua-pentafluorogermanate anions where these dimers and macrocyclic cations alternate [18].

In (**1**) the $[H_2DA18C6]^{2+}$ adopts the C_i conformation described by the following set of torsion angles, $(-g, -g, a, a, -g, a, -g, g, a)_2$ (Table 2). In the centrosymmetric dication there are four symmetry related angular fragments [19], in two of them two *gauche* bonds of the same sign meet at C(2) and C(2)$(-x, -y, -z - 1)$ atoms, while two *gauche*-bonds of the opposite sign meet at C(8) and C(8)$(-x, -y, -y, -z - 1)$ atoms. This strained conformation may be explained by the bridge function of the deprotonated oxime group which links two symmetry related nitrogen atoms of the macrocycle. More often in its complexes $[H_2DA18C6]^{2+}$ adopts a D_{3d} or C_i-conformation with two angular fragments differing in their position along the macrocyclic framework [15–17]. The distorted shape of the macrocycle is characterized by the pronounced deviations of the heteroatoms from the average plane which they define, O(1) 0.366(4), N(4) −0.467(1), O(7) 0.340(6) Å and the shortened distances between the trans-annular nitrogen atoms N(4)···N(4)$(-x, -y, -z - 1)$ 4.323(2) Å in comparison with the trans-annular distances between oxygen atoms, O(1)···O(1)$(-x, -y, -z - 1)$ 5.727(2), O(7)···O(7)$(-x, -y, -z - 1)$ 6.494(2) Å.

*Structure of (**2**)*

The independent part of the unit cell of (**2**) contains one macrocyclic cation $[DCH6A···NH_4]+$ and the (H-PTD)$^-$ monoanion linked together by H-bonds. The ORTEP drawing of (**2**) with the numbering scheme is depicted in Fig-

ure 4. The ammonium cation occupies the perching position and its nitrogen atom is displaced by 1.114(1) Å from the average plane of all oxygen atoms of the macrocycle. It affords three NH···O hydrogen bonds to three oxygen atoms, two of them, O(10) and O(16) being attached to the cyclohexyl rings, N···O distances N(1)···O(16) 2.909(1) Å, N(1)···O(10) 2.956(1) Å, and the central oxygen atom, N(1)···O(4) 2.950(1) Å. The ammonium cation is co-ordinated to the crown oxygens on the same side of the crown ether as two cyclohexyl substituents. A similar proximal arrangement was found for the metal and hydronium cations, K$^+$ [20], Tl$^+$ [21], Ba^{2+} [22], H$_3$O$^+$ [23], and for neutral molecules [24]. Some rare exceptions refer to complexes when bulky molecules such as the zwitter-ion of amidosulfuric acid, $^+NH_3SO_3^-$ [25], or the antimony trifluoride [26] molecule co-ordinates on the rear face of the macrocyclic cavity. The organization of each $[DCH6A·NH_4]^+$ cation in (**2**) strictly resembles it in the complex $[DCHA·NH_4](H_2O)I]_2$ [27].

In the same H-bonding mode as in (**1**), in (**2**) two (PTDH)$^-$ anions are linked into the centrosymmetric planar dimer, O(3G)···N(3G)$(-x + 1, -y + 1, -z)$ 2.803(1), O(3G)···O(4G)$(-x + 1, -y + 1, -z)$ 2.774(1) Å. These dimers are also combined into the chain through the pair of symmetry related NH···O interactions typical for barbiturate derivatives [10–13], N(1G)···O(1G)$(-x + 1, -y, -z - 1)$ 2.870(1) Å, R$_2^2$(8) graph set, Figure 5. *Via* its fourth hydrogen atom the ammonium cation is involved in the N(1)···O(4G) 2.720(1) Å interaction with the (H-PTD)$^-$ counterion and bridges the $[(PTDH)^-]_n$ chain and the attached macrocyclic molecules with the formation of the ribbon running along the [101] direction in the unit cell.

The DCHA conformation is described by the rather unusual set of torsion angles, $a, g\text{-}, g\text{-}, a, a, g, a, a, g\text{-}, g\text{-},$

Table 3. Hydrogen bonds in (**1**) and (**2**)

D—H···A, Å	d(D—H), Å	d(D···A), Å	D(D···A), Å	∠(DHA), deg
Complex (1)				
O(3G)—H(3G)···N(3G)^i	0.96(3)	1.91(3)	2.770(2)	148(2)
O(3G)—H(3G)···O(4G)^i	0.96(3)	2.11(2)	2.810(2)	128(2)
N(4)—H(1N4)···N(4G)	0.91(2)	2.00(2)	2.889(2)	166(2)
N(4)—H(1N4)···O(1G)	0.91(2)	2.46(2)	3.009(2)	119(2)
N(4)—H(2N4)···O(4G)^{ii}	0.91(2)	1.88(2)	2.742(2)	159(2)
N(1G)—H(1G)···O(7)^{iii}	0.84(2)	2.04(2)	2.881(2)	171(2)
Complex (2)				
N(1)—H(1N1)···O(16)	0.87(2)	2.04(2)	2.909(1)	172(2)
N(1)—H(2N1)···O(10)	0.90(2)	2.06(2)	2.956(1)	176(1)
N(1)—H(3N1)···O(4G)	0.96(2)	1.76(2)	2.720(1)	173(2)
N(1)—H(4N1)···O(4)	0.85(2)	2.11(2)	2.950(1)	166(2)
O(3G)—H(3G)···O(4G)^{iv}	0.86(2)	2.06(2)	2.774(1)	140(2)
O(3G)—H(3G)···N(3G)^{iv}	0.86(2)	2.09(2)	2.803(1)	140(2)
N(1G)—H(1G)···O(1G)^v	0.87(2)	2.00(2)	2.870(1)	175(1)

Symmetry transformations used to generate equivalent atoms: $i - x + 1, -y, -z; ii - x, -y, -z - 1; iii\ x, -y + 1/2, z + 1/2; iv - x + 1, -y + 1, -z; v - x + 1, -y, -z - 1$.
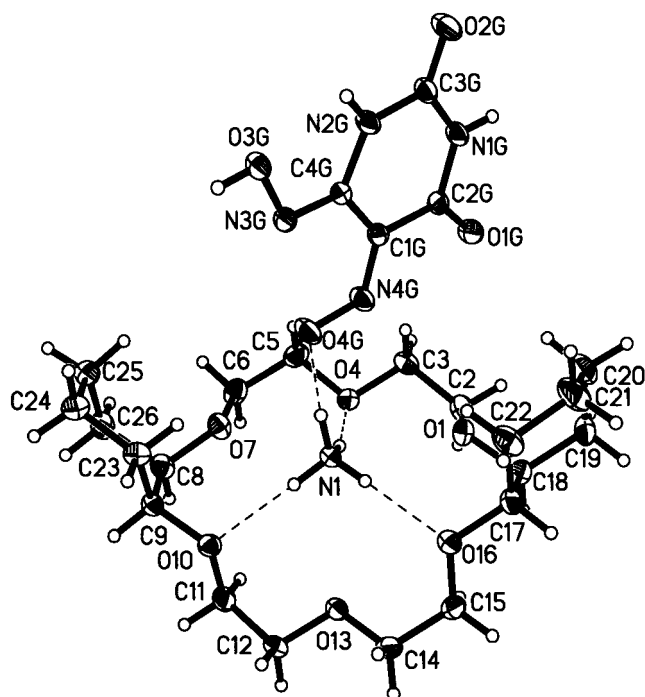

Figure 4. ORTEP drawing of (**2**) with atomic numbering scheme and hydrogen bonds shown as dotted lines. Non-hydrogen atoms are represented by thermal ellipsoids at 50% probability.
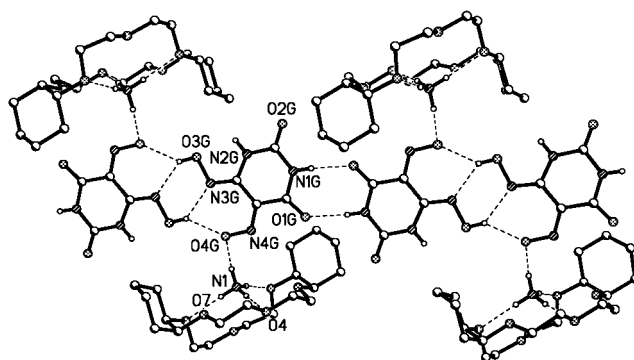

Figure 5. Ribbons in (**2**) running along [101] direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

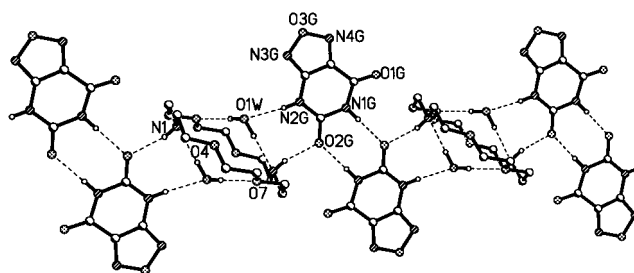*Figure 6.* Chains in (**3**) running along *c* direction. Hydrogen atoms of the crown-molecules are omitted for the sake of clarity.

a, *g-*, *a*, *a*, *g*, *a*, *g*, *g*, with three angular *gauche*, *gauche* fragments along the heterocyclic framework. The oxygen atoms of the macrocycle deviate essentially from their best plane, O(1), −0.156(1), O(4), 0.480(1), O(7), −0.324(1), O(10), −0.356(1), O(13), 0.901(1), O(16), −0.544(1) Å.

Structure of (3)

Complex (**3**) is built of the neutral molecules DA18C6, OPD and water in the ratio 1 : 2 : 2, as shown in Figure 6. The OPD and DA18C6 molecules in (**3**) are arranged in such

a way that the dihedral angle between the plane which includes all non-hydrogen atoms of the planar bicyclic OPD molecule and the plane of six oxygen atoms of the crown ring is 80.3(1)°.

A water molecule occupies the position above the macrocycle and acts as H-donor in two hydrogen bonds with the oxygen and nitrogen atoms of the crown-molecule, O(1w)···O(7)(−x + 1, −y + 1, −z + 1) 2.942(4), O(1w)···N(1) 3.023(5) Å, and as H-acceptor with OPD molecule, N(2G)···O(1w) 3.006(5) Å. The OPD molecule itself also has direct contact *via* the O(2G) carbonyl oxygen

atom with the NH-group of the macrocycle, N(1)$\cdots$O(2G) 2.720(5) Å. Two OPD molecules are combined into the planar dimer *via* a couple of symmetry related N—H$\cdots$O hydrogen bonds, N(1G)$\cdots$O(2G)($-x+1$, $-y$, $-z$) 2.901(4) Å, which as mentioned above, are typical for this class of compounds. The molecules in (**3**) are assembled into chains developed along the *c* direction in the unit cell.

The OPD molecule is characterized by a planar skeleton with the dihedral angle between the six-membered and diazole heterocycles equal to 1.00°. The conformation of the DA18C6 molecule is described by the ordinal D_{3d} symmetry typical for this molecule in the complexes with metal cations and in the uncomplexed state [28] with the C—C torsion angles in the range 67.8(4)–73.9(4)° and the maximal deviation of the C—O torsion angles from the open one being 3.2°.

Conclusions

For the first time the (4*Z*,5*E*)-pyrimidine-2,4,5,6(1*H*,3*H*)-tetraone-4,5- dioxime and the product of its cyclization, (1,2,5)-oxadiazolo(3,4-d)pyrimidine-5,7(4*H*,6*H*)-dione were prepared and the X-ray data obtained for their inclusion complexes with 18-membered crown ethers. H_2-PTD is stabilized in the form of the monoanion in the complex with diazonia-18-crown-6 and as ammonium salt in the complex with the *cis-syn-cis* isomer of dicyclohexano-18-crown-6.

The crucial factor in (**1**)–(**3**) is the mutual complementarity of donor and acceptor groups which provide the H-bonds responsible for the supramolecular architecture.

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