Full Articles

Nature of weak inter- and intramolecular interactions in crystals

7.* Stability of homochiral supramolecular organization of dications in crystals of 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one salts

Yu. V. Nelyubina,[a,b] K. A. Lyssenko,[a]★ A. S. Sigachev,[c] M. Yu. Antipin,[a] and A. N. Kravchenko[c]

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5085. E-mail: kostya@xray.ineos.ac.ru
[b]Higher Chemical College, Russian Academy of Sciences,
6 Miusskaya pl., 125820 Moscow, Russian Federation
[c]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5328. E-mail: sias@ioc.ac.ru

The geometries and peculiarities of the electronic structure of chiral 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one dications (C_2 symmetry) and their associates in salts containing chloride and nitrate anions were studied by X-ray diffraction analysis and quantum chemistry methods. Homochiral H-bonded cation chains are stable supramolecular fragments; however, their presence in the crystal structures does not provide spontaneous resolution of racemates upon crystallization.

Key words: 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-ones, X-ray diffraction studies, quantum chemical calculations, homochiral associates, cation-cation associates, spontaneous resolution.

Recently, crystal engineering has been widely used to obtain enantiopure compounds.[2] The method is based on spontaneous resolution of a racemate upon crystallization, namely, on the formation of a conglomerate (mechanical mixture of the right and left crystals), which can then be separated using different procedures.[3,4] Crystallographically, the formation of a conglomerate requires crystallization of the compound in one of 65 chiral space groups and the same chirality for all crystallographically independent molecules.[5] Otherwise, one can deal with the formation[5] of (1) true racemate (compound crystallizes in a racemic space group); (2) racemate (compound crystallizes in a chiral space group at $Z' > 1$ and enantiomer ratio of 1 : 1); (3) unbalanced racemate (compound crystallizes in a chiral space group at $Z' > 1$ and an enantiomer ratio different from 1 : 1, *i.e.*, here will be observed

---

* For Part 6, see Ref. 1.

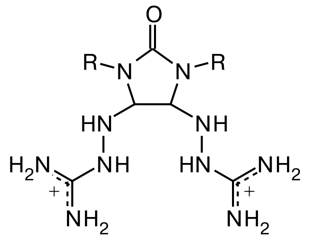
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 387—395, March, 2006.

ordered chiral crystals with a fractional enantiomeric excess); and (4) pseudoracemate (solid solutions of enantiomers); here the compound crystallizes in a chiral space group at $Z' \geq 1$ and random disorder (superposition of enantiomers).

Thus, performing spontaneous resolution is a rather complicated task, which can not always be done. However, it is believed that by choosing particular functional groups it is possible to attain the formation of a chiral molecular associate and, as a result, spontaneous resolution.[2—4] In the case of organic compounds the most promising way is to design H-bonded chiral associates.[5] Using this approach, it was possible to separate, *e.g.*, enantiomers in a series of glycol uril derivatives.[6] However, a study of 4-{3,7-dioxo-2-(3-carboxypropyl)-6,8-dialkyl-2,4,6,8-tetraazabicyclo[3.3.0]oct-2-yl}butane acids showed that in spite of the formation of chiral H-bonded layers in the 6,8-dimethyl and 6,8-diethyl derivatives, spontaneous resolution was observed only for the former compound.[6d] Therefore, the formation of a chiral associate can be considered a necessary rather than sufficient condition for spontaneous resolution.

Based on this, it was interesting to analyze whether homochiral associates observed upon spontaneous resolution in other classes of compounds are retained in racemic crystals. In other words, we were interested in assessing the stability of these associates and, therefore, their significance for spontaneous resolution of enantiomers.

In this work we studied 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one salts based on dications **1a,b**. The choice of the compounds is due to the fact that crystallization of racemate 1,3-dimethyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one dihydrochloride dihydrate is followed by spontaneous resolution (space group $P6_1$).[7]



1a,b

R = Me (**a**), Et (**b**)

In the crystal, translational chiral chains comprised of dications **1a** are held together through N—H...O bonds while anions and solvate water molecules link the homochiral chains to form a three-dimensional H-bonded framework. The presence of numerous proton donors and acceptors in this dication suggests that a minor structural change, *e.g.*, variation of substituents at nitrogen atoms of imidazolidin-2-one or replacement of anion will result in another type of supramolecular organization of dications in the crystal. In order to study the effects of these factors on the character of supramolecular organization of dications in the crystal, we carried out an X-ray diffraction study of salts **2—5** of the 1,3-dimethyl (**1a**) and 1,3-diethyl (**1b**) derivatives of 4,5-bis(3-guanidinioamino)imidazolidin-2-one with the chloride (**2** and **4**, respectively) and nitrate (**3** and **5**, respectively) anions (Fig. 1). The data for salt **2** are listed for comparison.

Results and Discussion

Unlike salt **2**, the other salts studied crystallize in racemic space groups (Table 1). Chloride **4** crystallizes as a hydrate containing three water molecules per dication. Based on the unit cell parameters, salts **3** and **5** are isostructural and contain no solvate molecules. However, the type of the cation-cation associate in these nitrates appeared to be identical to that found in salt **2** (Fig. 2), which is quite unexpected.

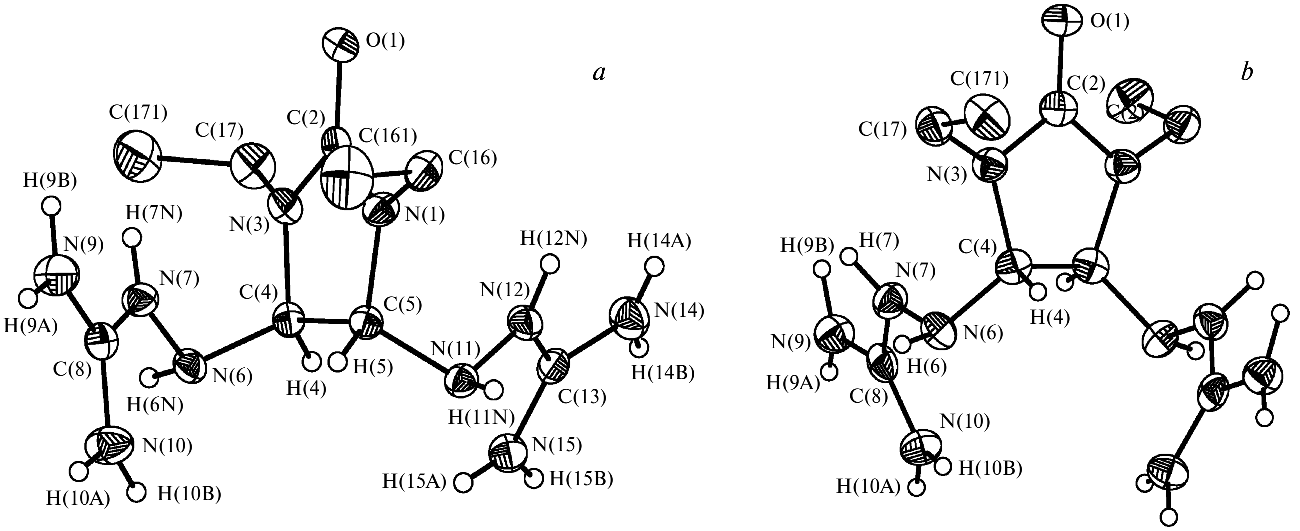


Fig. 1. General view of dications **1b** in salts **4** (*a*) and **5** (*b*). The atomic numbering scheme for dication **1a** is the same as that for the dication of salt **4**.

Table 1. Key crystallographic data and refinement parameters for salts **3**—**5**

Parameter	**3**	**4**	**5**
Empirical formula	$C_7H_{20}N_{12}O_7$	$C_9H_{30}Cl_2N_{10}O_4$	$C_9H_{24}N_{12}O_7$
Molecular weight	384.35	413.33	412.40
T/K	120	298	120
Crystal system		Monoclinic	
Space group	$C2/c$	$P2_1/c$	$C2/c$
Z (Z')	4 (0.5)	4 (1)	4 (0.5)
a/Å	13.208(2)	11.387(2)	14.832(1)
b/Å	7.3837(1)	14.971(3)	7.4587(8)
c/Å	16.025(3)	12.347(3)	16.901(2)
β/deg	92.371(4)	98.96(3)	102.480(4)
V/Å^3	1561.5(5)	2079.2(7)	1825.5(3)
d_{calc}/g cm^{-3}	1.635	1.320	1.501
μ/cm^{-1}	1.42	3.47	1.27
F(000)	808	880	872
2θ$_{\text{max}}$/deg	60	64	58
Number of measured reflections	5482	7790	4577
Number of independent reflections	2252	7521	2299
Number of reflections with $I > 2\sigma(I)$	1315	4847	1249
Number of parameters to be refined	159	347	176
R_1	0.0570	0.0494	0.0524
wR_2	0.1223	0.1349	0.1108
GOOF	1.074	1.033	1.063
Residual electron density (d_{min}/d_{max})/e Å^{-3}	0.34/−0.278	0.513/−0.677	0.229/−0.371

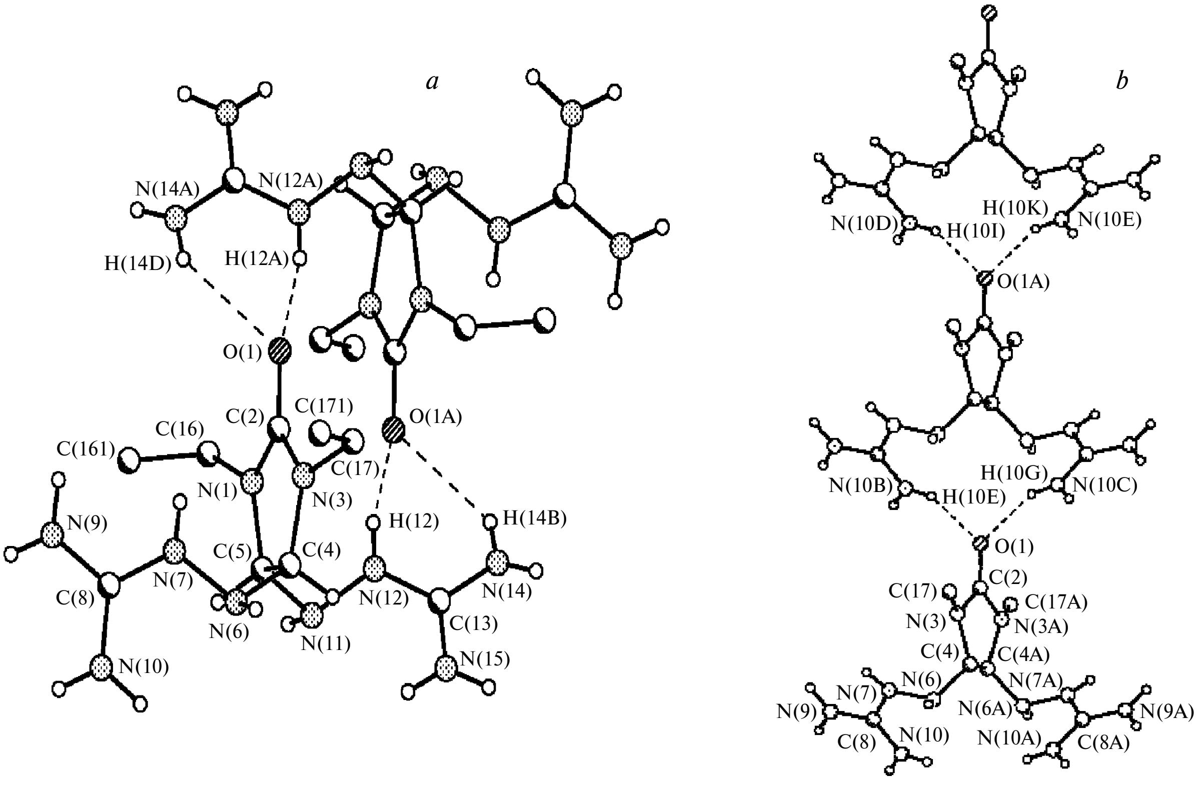


Fig. 2. N—H...O-bonded dimer in the crystal of compound **4** (*a*) and N—H...O-bonded translational chain in crystals **2**, **3**, and **5** (*b*). The second dication in the dimer was obtained from the first one by symmetrical transformation $-x + 1$, $-y$, $-z + 2$.

Clearly, the character of intermolecular interactions in the salts under study depends not only on the nature of the anion but also on peculiar features of the geometry of dications. Therefore, prior to discussing the supramolecular organization in the crystal, we will consider how the structure of the dications varies depending on the nature of substituents at nitrogen atoms and anions. In order to establish how intermolecular interactions influence the geometry of dications **1a,b** in the crystal, we also carried out B3LYP/6-31G** quantum chemical calculations of these dications.

Structure of dications 1a,b. In all salts the dications have C_2 symmetry and *trans*-arrangement of 3-guanidinioamino (GuaNH$_2$) substituents. In salts **3** and **5**, the dication is on the C_2 axis passing through the carbonyl group and the midpoint of the C—C bond in the ring. Thus, in these structures the limiting symmetry of dication is the same as the position symmetry.

In the crystals of the salts under study, imidazolidin-2-one adopts a *twist*-conformation in which the C(4) and C(5) (or C(4) and C(4A)) atoms deviate by a distance of d_C from the plane of the amide fragment. In the systems with the diethyl dication **1b** the ring is systematically flattened with a minimum d_C value for the crystal of compound **4**. One can assume that differences between the five-membered ring conformations in structures **4** and **5** are due to the mutual arrangement of Et groups at the N(1) and N(3) atoms. In the crystal of compound **4** the Et groups are on the same side with respect to the midplane of the five-membered ring, whereas in salt **5** the substituents at nitrogen atoms are arranged in *trans*-fashion. However, B3LYP/6-31G** calculations of isolated dication **1b** showed that the geometries and energies of two isomers of this species with *cis*- and *trans*-arrangement of the Et groups are almost the same (energy difference is 0.12 kcal mol^{-1}). Thus, the mutual arrangement of the ethyl substituents in salts **4** and **5** is mainly determined by the crystal packing effects rather than intramolecular steric repulsion between these groups. On going from crystal to isolated dications the five-membered ring is flattened.

Experiments show an appreciable ring flattening in the crystal of compound **4**. But, according to calculations of isolated dications, this causes the degree of pyramidalization of the N(1) and N(3) atoms to change. For instance, the deviation of the N(1) and N(3) atoms (d_N) from the plane passing through carbon atoms bound to these nitrogens in structure **4** (0.07—0.10 Å) is nearly half as large as the corresponding parameters of other structures (0.22—0.26 Å). For comparison, the isolated dications are characterized by d_N values of 0.15 Å (**1a**) and 0.13 and 0.17 Å (both for **1b**) depending on the arrangement of Et groups (see above).

The bond length distribution in the amide fragment, $N_2C{=}O$, depends only slightly on the nature of the substituent at the ring N atoms. Mention may be made of a slight elongation of C—N bonds in nitrates (Table 2). It becomes more significant for the gas phase, being likely due to both an increase in polarity of the medium and specific solvation (see below).

The N(11)—C(5)—C(4)—N(6) torsion angle characterizes the mutual arrangement of GuaNH$_2$ substituents in the salts with homochiral H-bonded translational chains (**2**, **3**, **5**). Irrespective of the nature of the anion and substituents at the N(1) and N(3) atoms it varies only slightly (82.4—89.2°), but reaches 122.9° for **4**. B3LYP/6-31G** calculations of dications gave a N(11)—C(5)—C(4)—N(6) torsion angle of 113.5° for **1a** and 112.5° for **1b**.

Analysis of the bond lengths in the GuaNH$_2$ fragment showed that, in spite of a large number of H-bonds that are formed by this fragment, only the bond lengths in

Table 2. Key geometric parameters of dications in salts **2—5** according to data of X-ray diffraction experiments and B3LYP/6-31G** calculations[a]

Parameter/Å	**2**	**3**	**4**	**5**
d_C[b]	0.198(9)/0.191(9) [0.0002/0.0004]	0.202(6) [0.0002/0.0004]	0.092(6)/0.077(6) [0.013/0.013]	0.167(5) [0.013/0.013]
d_N[c]	0.223(8)/0.223(7) [0.155/0.155]	0.261(5) [0.155]	0.069(4)/0.102(4) [0.1315/0.1748]	0.227(3) [0.1719/0.1719]
C(2)—N(1)/ C(2)—N(3)	1.360(9)/1.364(9) [1.399]	1.369(3) [1.399]	1.360(2)/1.360(2) [1.400]	1.371(2) [1.400]
N(1)—C(5)/ N(3)—C(4)	1.465(6)/1.463(6) [1.440]	1.451(3) [1.440]	1.447(2)/1.454(2) [1.440]	1.461(3) [1.440]

[a] The values obtained from B3LYP/6-31G** calculations are given in square brackets.

[b] Deviation of the C(4)/C(5) atoms (salts **2** and **4**) or the C(4)/C(4a) atoms (salts **3** and **5**) from the plane of the amide fragment in the dication.

[c] Deviation of the N(1)/N(3) atoms from the plane passing through carbon atoms bound to these nitrogen atoms. The results of calculations for structures **4** and **5** correspond to *cis*- and *trans*-arrangement of Et groups, respectively.

$C(NH_2)_2$ groups are changed, whereas the N—N bond lengths in the crystals of the salts (1.395(7)—1.407(2) Å) and in isolated dications (1.405 Å) are almost the same. In salt **3** and in one $C(NH_2)_2$ group of crystal **4** the C—N bonds are equalized, but in the other $C(NH_2)_2$ groups one C—N bond (1.302(3)—1.312(2) Å) is systematically shorter than the other bond (1.325(7)—1.333(2) Å). It should be noted that elongation of C—N bonds was obtained for the NH_2 group that forms both stronger and weaker H-bonds compared to those formed by the adjacent NH_2 group. For comparison, the C—N bond lengths in the $C(NH_2)_2$ fragments of isolated dications **1a** and **1b** are almost indistinguishalbe, being equal to 1.330 and 1.335 Å, respectively.

The conformation of the $GuaNH_2$ fragment in the salts is also rather stable. Indeed, in spite of different number and strength of the H-bonds formed by the NH group the corresponding H—N—N—H torsion angle varies between 39.9° and 69.2° (*cf.* 71.9° for **1a** and 73.7° for **1b** obtained from B3LYP/6-31G** calculations). Conformational stability can be due to different reasons. First, the N(7) and N(12) atoms are likely involved in conjugation with the $C(NH_2)_2$ group, as indicated by the "flattening" of the N atom and shortening of the C(8)—N(7) and C(13)—N(12) bonds to ~1.333 Å. Second, the lone electron pairs (LPs) of the N(6) and N(11) atoms are probably involved in anomeric interaction, that is, charge transfer from the LPs to the antibonding orbitals of two ring bonds, C(4)—N(3) and C(5)—N(1). Indeed, the last assumption is substantiated by the values of the LP-N(6)—C(4)—N(3) pseudotorsion angle (166—169°). We can also not exclude the presence of an intramolecular H-bond N(11)...H(15B)—N(15), which thus closes the five-membered ring characterized by average N...H and N...N distances of 2.36 and 2.49 Å, respectively, and an N—H...N angle of 104°.

Topological analysis of the electron density distribution function $\rho(\mathbf{r})$ carried out in the framework of the "Atoms in molecule" theory[8] and analysis of localized orbitals in the framework of the NBO approach[9] performed for dications **1a,b** confirmed the assumptions mentioned above.

For instance, the ellipticities at the (3, −1) critical points of the C—N bonds in the $N—C(NH_2)_2$ group are almost the same, being equal to 0.20—0.21, which unambiguously indicates delocalization of the π-electron density over all three C—N bonds in the fragment. Our NBO analysis confirmed the occurrence of the anomeric effect, namely, the energy of the anomeric interaction between the LPs of the N(6)/N(11) atoms and the σ*-orbitals of the C(4)—N(3)/C(5)—N(1) bonds are 8.0 kcal mol^{-1}. This type of charge transfer is also indicated by the corresponding bond ellipticities.

The formation of a five-membered N...H—N-bonded ring immediately follows from the presence of a (3, −1) critical point in the interatomic space. Apparently, it is the H-bond that is responsible for a slight elongation of one C—N bond in isolated dications (see above). The energy of the intramolecular H-bond, estimated based on a semiquantitative dependence of this parameter on the potential energy density at the (3, −1) critical point,[10] is 4.15 kcal mol^{-1}. However, the closed five-membered ring is relatively unstable. Indeed, the distance between the (3, −1) critical point of the H-bond and the (3, +1) critical point of the H-ring is 0.24 Å and, therefore, minor changes in the torsion angles can cause "coincidence" of these points (bifurcation),[8] which leads to "disappearance" of the H-bond and to a change in the molecular graph.

In order to evaluate the charge distribution in dications, the $\rho(\mathbf{r})$ function was integrated over their atoms, *i.e.*, over the subspace bound by the zero-flux surface.[8,11] Analysis of the atomic charges based on the results of B3LYP/6-31G** calculations showed that the maximum negative charge is localized on the amido group, while $C(NH_2)_2$ groups are positively charged. Comparison of the charges in the dimethyl and diethyl dications shows that the charges of the $C(NH_2)_2$ and amido groups are similar in absolute values, being equal to 1.22 and −1.65 e, respectively. Such a charge separation in the dication seems to be responsible for the formation of cation-cation associates that are quite rare to occur in crystals.

Thus, analysis of the geometry and electronic structure of dications in the crystal and in the gas phase shows that variation of substituents at the ring nitrogen atoms has little effect on their geometry.

Crystal packing. Analysis of the packing in crystals **2—5** revealed not only cation-anion but also cation-cation and anion-anion interactions in all structures. Now we will consider each type of supramolecular organization in the salts under study in more detail.

The crystals of salts **3** and **5** include centrosymmetrical dimers formed by NO_3^- anions, in which one oxygen atom of the nitrate is "projected" on the nitrogen atom of the adjacent anion. Their parameters differ insignificantly, namely, the intermolecular N...O distances in **5** and **3** are 2.957(2) and 3.179(2) Å, respectively, and the N—O...N angles, which characterize the directionality of the contact, are 97.6(1) and 102.7(1)°, respectively. However, quantum chemical calculations of $(NO_3)_2^{2-}$ dimer showed that geometry optimization leads to a considerable increase in the O....N interatomic distance up to infinity, which indicates a forced character (effect of the crystal packing) of this anion-anion interaction.

Another situation is characteristic of the compounds with chloride anion. In these salts, it is impossible to selsct direct anion-anion interactions, but both crystals (**2** and **4**) contain similar associates that are formed by water molecules and Cl^- anions. In the crystal of salt **2**, two solvate water molecules and two Cl^- anions

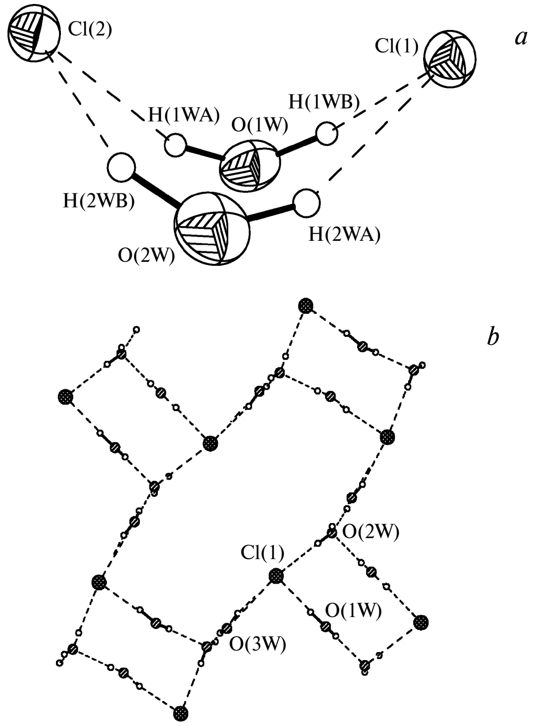


Fig. 3. Chlorohydrate associates: four-membered ring in crystal **2** (*a*) and a layer in crystal **4** (*b*).

alternate, thus forming a nonplanar four-membered ring with O...Cl distances of 3.054(6)—3.231(6) Å (Fig. 3, *a*). Contrary to this, the crystal of salt **4** (solvate with three water molecules) is built of infinite H-bonded puckered layers formed by Cl$^-$ ions and water molecules (Cl(1)...O(2W), Cl(1)...O(1W), and O(1W)...O(2W) distances are 3.090(2), 3.172(2), and 2.838(2) Å, respectively). These layers comprise a six-membered ($[Cl(H_2O)_2]_2$) ring in the chair conformation and a fourteen-membered ($[Cl(H_2O)_2Cl(H_2O)_3]_2$) ring in the chair—boat conformation that share an edge (see Fig. 3, *b*). Large rings are "threaded" with dimeric dications of the ethyl derivative **4** (see below). The shortest interatomic distances Cl...Cl in the crystals of salts **2** and **4** are 4.12 and 6.72 Å, respectively.

Table 3. Geometric characteristics of intermolecular H-bonds in dication chains of salts **2**, **3**, and **5**

Parameter	**2**	**3**	**5**
Bond		*d*/Å	
O(1)...N(10)/	2.800(8)/	2.911(3)	2.8639(2)
O(1)...N(15)*	2.802(8)		
O(1)...H(10B)/	1.86/	2.08	2.12
O(1)...H(15B)	1.87		
Angle		ω/deg	
O(1)...H(10B)...N(10)/	153	155	147
O(1)...H(15B)...N(15)			
H(10B)...O(1)...H(15B)	106	99.6	116

* The N—H distances were normalized to the values obtained from B3LYP/6-31G** calculations of isolated dications.

Table 4. Geometric parameters of H(12)...O(1)...H(14B) intermolecular bond in the crystal of compound **4** obtained from X-ray diffraction experiment (XRD) and from B3LYP/6-31G** quantum chemical calculations

Parameter	XRD	B3LYP/6-31G**
Bond	*d*/Å	
O(1)...N(12)*	2.763(2)	3.037
O(1)...N(14)	3.180(2)	2.896
O(1)...H(12)	1.79	2.14
O(1)...H(14B)	2.33	1.95
Angle	ω/deg	
O(1)...H(12)...N(12)	161	146
O(1)...H(14B)...N(14)	141	153
H(12)...O(1)...H(14B)	51	66

* The N—H distances were normalized to the values obtained from B3LYP/6-31G** calculations of isolated dications.

In spite of basically different nature of anions and the character of the anion-anion associates, cation-cation associates are more stable. For instance, in salts **2**, **3** and **5** the dications are linked through N—H...O bonds, thus forming homochiral translational chains (see Fig. 2, *b*); centrosymmetrical dimers are formed only in chlorohydrate **4** (see Fig. 2, *a*). The data in Tables 3 and 4 show that in both types of cation associates the dication forms four H-bonds of comparable strength (evaluation based on the N...O distance). The role of proton acceptor is played by the carbonyl group that forms two H-bonds. Possible proton donors are either only NH_2 groups or the NH_2 and NH groups in chains and dication dimers, respectively. Probably, different nature of proton donor makes the bifurcate bond formed by the C=O group in chains in the crystals **2**, **3**, and **5** symmetric, whereas in dimers the N—H...O bond with the NH group is much stronger.

The geometric characteristics of the H-bond that links dicationic salts **3** and **5** to form homochiral translational chains differ insignificantly (see Table 3). Comparison with the parameters of salt **2** shows that in all three salts the O...N distances responsible for the strength of the H-bonds change in a rather narrow range from 2.800(8) to 2.911(3) Å (see Table 3). Analysis of the charges on the carbonyl group in dications **1a,b** (see above) shows that the nature of substituent has no effect on the strength of the bifurcate H-bond. It should be emphasized that in racemates **3** and **5** the homochiral chains are arranged in an antiparallel motif, whereas in salt **2** the chains make an angle of 60°.

Note that, according to quantum chemical calculations, the isolated homochiral and heterochiral cation associates are characterized by basically different stability. For instance, qualitative characteristics of the H-bond in the crystalline dimer **4** are also retained in the gas phase (see Table 4). The bond formed by the NH_2 group is stronger in spite of equalization of two components of the bifurcate H-bond in isolated dimer. It should be emphasized that in the dimer the geometry of the dication (especially its amide fragment) is much more similar to experimental data. In particular, the N—C bond lengths are 1.375—1.377 Å.

On the contrary, homochiral associate appears to be unstable in the gas phase. For instance, optimization of homochiral dimers and corresponding trimers leads to infinitely long distance between dications. Our analysis of the $\rho(\mathbf{r})$ topology in dimer **1b** showed that both components of the bifurcate H-bond correspond to attractive interactions. The energy of H-bonds per molecule estimated from the dependence[10] mentioned above is 9.8 kcal mol^{-1}. Taking into account similarity in the H-bond parameters for chains and dimer, one can suggest that the chain H-bonds also have a rather high energy.

Instability of isolated homochiral chains suggests that cation-anion interactions contribute largely to their stabilization. Indeed, analysis showed that in salts **2** and **5** the four-membered chlorohydrate rings and NO_3^- anions form H-bonds with dications, thus acting as chain segment linkers (Figs 4 and 5).

Salt **3** is formally isostructural to salt **5**. But in spite of the presence of homochiral chains, in **3** the nitrate anion does not act as a linker and forms H-bonds only with a dication within the same homochiral chain. Thus, the example of the nitrate anions clearly illustrates that the presence of an additional linker is not necessary for stabilization of homochiral chains.

Parameters of the cation—anion H-bonds in salts **3** and **5** are almost the same. In both salts the nitrate anion forms six H-bonds with N...O distances lying in the range 2.899(3)—3.187(3) for **3** and 2.884(3)—3.297(3) Å for **5**. Besides, the number of anions that interact with one chain dication in compounds **3** and **5** is different (six and eight, respectively). Thus, the number of anions in the solvation shell of dication **1b** in salt **5** increased despite the increase in hydrophobicity. For comparison, the number of four-membered chlorohydrate rings that form H-bonds with one dication in salt **2** equals six.

Therefore, although substituents at the N(1) and N(3) ring atoms form no shortened contacts and thus have no direct effect on the character of the packing of dications in salts **3** and **5**, their steric effects are strong enough to favor realization of various cation-anion interactions in the crystals of salts.

Thus, our analysis of four crystal structures containing 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one dications with C_2 symmetry showed that homochiral chains in conglomerate **2** are rather stable; they are retained upon variation of both the substituents at nitrogen atoms and the anion.

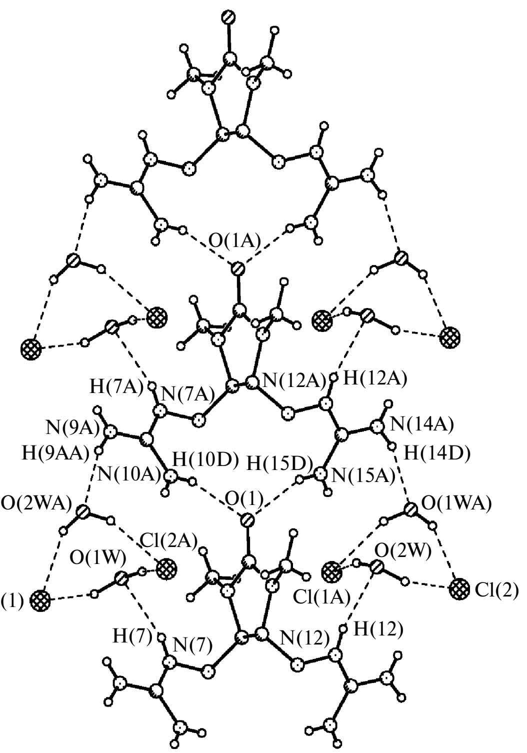


Fig. 4. N—H...O-bonded translational chain in crystal **2**. Here and in Fig. 5 some nitrate anions and chlorohydrate rings that form H-bonds with the cation chains are not shown. Dications in the chain were obtained from the basis cation by symmetry transformation $x, y + 1, z$.

The type of supramolecular organization of dications in the crystals of 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one salts studied in this work (homochiral chains or centrosymmetrical dimers) seems to be dependent on which process (formation of cation-cation or anion-anion associates) predominates. In particular, it is highly probable that the driving force for crystals **2**, **3**, and **5** is the cation-cation association while in **4** this is the formation of chlorohydrate associates and subsequent self-assembly of dications.

A change in chirality of the crystal (homochiral chloride **2** *vs.* racemic nitrates **3** and **5**) is likely due to anion-anion interactions. Indeed, in the absence of direct contacts between cation chains the chirality of a nitrate crystal is determined by the centrosymmetrical dimers $NO_3^-...NO_3^-$ for which the interaction energy is *a priori* lower than the energy of H-bonds in cation chains.

Thus, similarly to the previous communication,[6d] this study showed that in the case of homochiral packing the role of strong intermolecular H-bonds and associates formed involving them is, by and large, to some extent stretched. Indeed, almost uncontrollable weak interac-

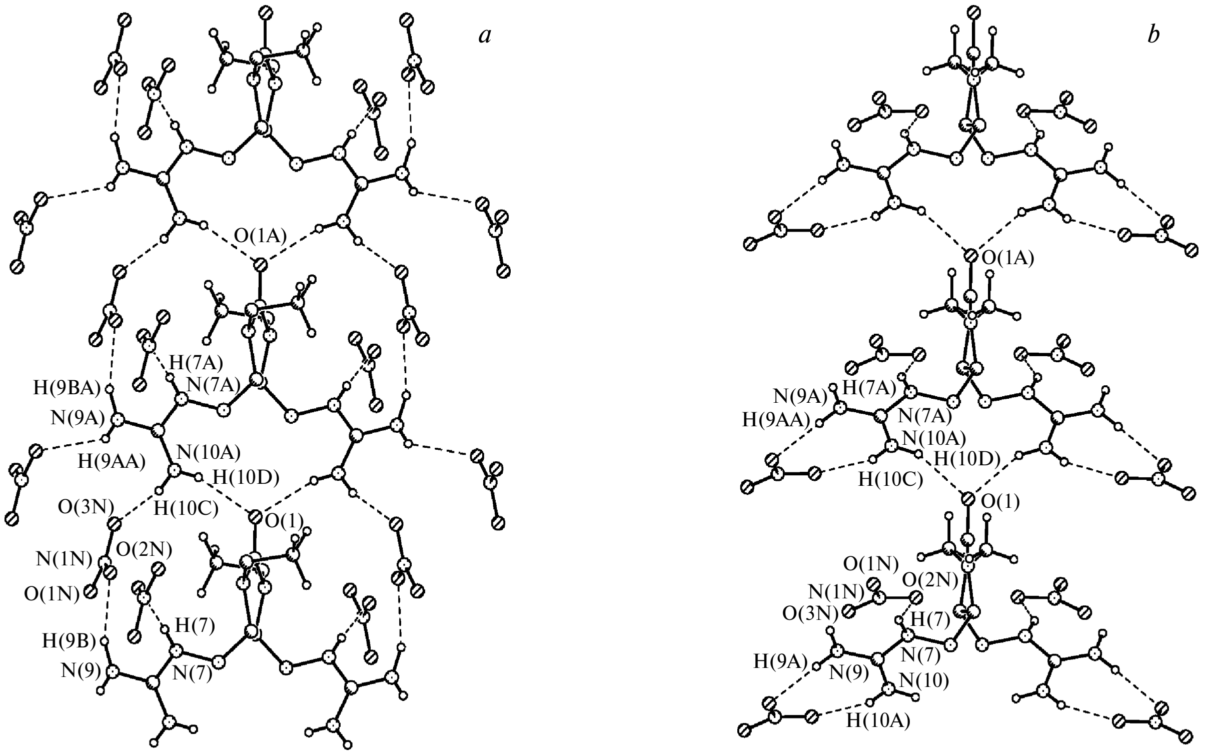


Fig. 5. N—H...O-bonded translational chain in crystals **5** (*a*) and **3** (*b*). Dications in the chains were generated from the basis cations by symmetry transformation $x, y + 1, z$ (*a*) and $x, y - 1, z$ (*b*).

tions can and do play the key role in stabilization of racemic and homochiral crystals.

Experimental

X-Ray diffraction studies were carried out with a SMART 1000 CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scan technique) compounds **3** and **5** and with a Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scan technique) for compound **4**. The structures were solved by the direct method and refined using the least squares method anisotropically in the full-matrix approximation with respect to F^2_{hkl}. Hydrogen atoms were located from the difference Fourier syntheses of the electron density and then refined isotropically. The key crystallographic data and refinement parameters for the structures under study are listed in Table 1. All calculations were carried out using the SHELXTL program package.[12]

Quantum chemical calculations of dications **1a,b** and cation-cation associates were carried out using the GAUSSIAN98 program,[13] the B3LYP functional, the 6-31G(d,p) basis set, and the results of the X-ray diffraction experiments as the starting geometry. The standard errors of $4.5 \cdot 10^{-4}$ and $1.8 \cdot 10^{-3}$ a.u. for the maximum force and displacement, respectively, were set as convergence criteria. Topological analysis of the function ρ(**r**) was carried out using the MORPHY 98 program[14] with the wave function obtained from B3LYP calculations.

Synthesis of 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one dihydrochlorides 2 and 4. To a solution of 1,3-dimethyl- or 1,3-diethyl-4,5-dihydroxyimidazolidin-2-one (0.02 mol) and aminoguanidine hydrochloride (0.04 mol) in 20 mL of methanol, conc. hydrochloric acid (0.2 mL) was added dropwise and the mixture was stirred at 70—75 °C for 1 h. The reaction mass was kept in a refrigerator for ~14 h. The precipitate (salts **2** and **4**) was filtered off and crystallized from methanol. The physicochemical characteristics of the compounds obtained were in agreement with the published data.[7]

Synthesis of 1,3-dialkyl-4,5-bis(3-guanidinioamino)imidazolidin-2-one dinitrates 3 and 5. To a solution of 0.02 mol of salt **2** (**4**) in 5 mL of water, $AgNO_3$ (0.04 mol) was added and the mixture was stirred at ~20 °C for 1 h. The AgCl precipitate was filtered off. The stock solutions were kept at ~20 °C for 10 h. Precipitated crystals of **3** (**5**) were filtered off.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 06-03-32557), the Council on Grants at the President of the Russian Federation (Program for the State Support of Young Russian Researchers, Grant MK-1054.2005.3), and the Foundation for Support of Russian Science.

References

1. K. A. Lyssenko, D. V. Lyubetskii, M. Yu. Antipin, and I. L. Odinets, *Izv. Akad. Nauk. Ser. Khim.*, 2005, 2406 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 2484].
2. L. Perez-Garcia and D. B. Amabilino, *Chem. Soc. Rev.*, 2002, **31**, 342.

3. J. Jacques, A. Collet, and S. H. Wilen, *Enantiomers, Racemates, and Resolution*, Krieger Publ. Comp., Malabar (Florida), 1994.
4. *Mendeleev Commun.*, Special Issue, 2003, 85.
5. H. D. Flack, *Helv. Chim. Acta*, 2003, **86**, 905.
6. (a) R. G. Kostyanovsky, K. A. Lyssenko, G. K. Kadorkina, O. V. Lebedev, A. N. Kravchenko, I. I. Chervin, and V. R. Kostyanovsky, *Mendeleev Commun.*, 1998, 231; (b) R. G. Kostyanovsky, K. A. Lyssenko, A. N. Kravchenko, O. V. Lebedev, G. K. Kadorkina, and V. R. Kostyanovsky, *Mendeleev Commun.*, 2001, 134; (c) R. G. Kostyanovsky, G. K. Kadorkina, K. A. Lyssenko, V. Y. Torbeev, A. N. Kravchenko, O. V. Lebedev, G. V. Grintselev-Knyazev, and V. R. Kostyanovsky, *Mendeleev Commun.*, 2002, 4; (d) K. A. Lyssenko, D. G. Golovanov, A. N. Kravchenko, I. E. Chikunov, O. V. Lebedev, and N. N. Makhova, *Mendeleev Commun.*, 2004, 105.
7. A. N. Kravchenko, G. K. Kadorkina, A. S. Sigachev, E. Yu. Maksareva, K. A. Lyssenko, P. A. Belyakov, O. V. Lebedev, O. N. Kharybin, N. N. Makhova, and R. G. Kostyanovsky, *Mendeleev Commun.*, 2003, 114.
8. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.
9. A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
10. E. Espinosa, E. Mollins, and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.
11. R. F. W. Bader and C. F. Matta, *J. Phys. Chem. A*, 2004, **108**, 8385.
12. G. M. Sheldrick, *SHELXTL-97, Version 5.10*, Bruker AXS Inc., Madison (WI, USA), 1997.
13. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *GAUSSIAN98, Revision A.7*, Gaussian, Inc., Pittsburgh (PA), 1998.
14. (a) P. L. A. Popelier and R. G. A. Bone, *MORPHY98, a Topological Analysis Program*, UMIST (England), 1998; (b) P. Popelier, *Chem. Phys. Lett.*, 1994, **228**, 160.

Received September 22, 2005;
in revised form January 20, 2006