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Supramolecular aggregation by means of charge-assisted hydrogen bonds in acid-base adducts containing amidinium cations

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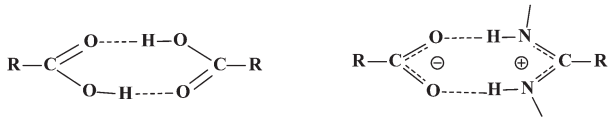
Amidinium cations are molecular building blocks widely used in crystal engineering studies in view of their capacity to form strong and directional charge-assisted N–H···O bonds. The X-ray crystallographic structures of three acid-base complexes, amidinium–acetate and amidinium–(2-hydroxyethoxy)acetate in two polymorphic forms, are reported, together with a systematic analysis of acid-base adducts containing amidinium cations found in the Cambridge Crystallographic Database. A detailed discussion on the preferred packing patterns adopted by these adducts shows that the supramolecular synthon characterized by a dimeric coupling of RN^+–H and O^- functionalities *via* an O···H bond is highly conserved and dominates the crystal's three-dimensional arrangement. Calculations of the two polymorphs' crystal energies revealed that the total energy difference between the polymorphs is less than 1 kcal mol^{-1}, H-bonding contributions being strictly comparable and the main difference being imputed to van der Waals and angular and torsional intramolecular terms, in agreement with the fact that in the two crystals the flexible anion adopts completely different conformations. This is in keeping with the idea that, for an '*a priori*' predictability of crystal packing motifs, it is important not only to perfectly match the number of H-bond donors and acceptors but also to have a relative rigidity of the molecular fragments constituting the co-crystal.

Introduction

Intermolecular interactions are the basis for crystal engineering, their nature and strength determining their relative importance in forming different crystal packings. Among these forces, hydrogen bonds are the most important in view of their higher energy and directionality and, accordingly, their properties have been extensively utilized in the planning of crystal adducts of molecules or ions having complementary acceptor and donor sites. It has been observed that the strength of these directional forces, and consequently their ability to control the formation of intermolecular aggregates, depends on the nature and polarity of the donor and acceptor groups and becomes very high when the hydrogen bond is assisted by resonance or by charge.[1] The most used and maybe easiest way to take advantage of this type of strong interactions to obtain crystals of predictable packing patterns is the co-crystallization of acids and bases with complementary functional group. Actually, many papers have been published on this topic in the last few years, for example on dioximes and oxamate salts,[2] amine oxalates,[3] dicarboxylic acids and amines,[4] squarates,[5] *etc.*

From the point of view of the potential use of a specific class of molecules as building blocks of H-bonded architectures for crystal engineering, amidinium ion and its derivatives appear to be very promising, as they easily form acid-base complexes with carboxylate or other oxygenate anions, which are linked by strong N^+–H···O^- (±) Charge-Assisted H-Bonds (CAHB).[6] They usually are arranged in a 'dimeric' motif similar to that found in carboxylic acid dimers (Scheme 1), which can be called a 'supramolecular synthon' according to Desiraju.[7]

This particular synthon, for instance, was successfully used by Hamilton and coworkers to build up synthetic receptors able to selectively recognize dicarboxylic acids.[8] Accordingly, several structural papers have been published on amidinium complexes and a relevant number of different crystal structures containing their complexes are available in the Cambridge Structural Database (CSD).[9]



Scheme 1

A CSD search on all amidinium ion/oxygenate anion complexes has been performed and an analysis of the observed structural motifs is reported in the present paper in order to obtain more information on the probability of formation, or the recurrence frequency, in relation with the structural features of the molecules involved. Together with this comparative analysis of packing modes, we present here three new crystal structures of amidinium complexes: amidinium/acetate and amidinium/(2-hydroxyethoxy)acetate, the last one crystallizing in two polymorphic forms, which is an example of *conformational polymorphism* according to Bernstein's definition,[10] because of '*the existence of different conformers of the same molecule* (in this case the anion) *in different polymorphic modifications*'.[10] Moreover, the lattice energies of the two polymorphs have been evaluated in order to obtain a deeper insight into the relative importance of the contribution of the different intermolecular forces involved (van der Waals, hydrogen bonding, Coulombic) to the total packing energies.

Results

Description of the structures

Suitable crystals for X-ray analysis of the complexes of amidinium–acetate (**1**) and amidinium–(2-hydroxyethoxy)acetate

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form I (**2**) and form II (**3**) were obtained by recrystallization (see Experimental for details). ORTEP[11] views of the three complexes are shown Fig. 1 and Table 1 reports the geometrical parameters of the intra- and intermolecular hydrogen bonds. Figs. 2–4 show their most characteristic packing arrangements.

In all the three structures the acid-base adducts are linked by two N–H···O (±) charge-assisted hydrogen bonds (Table 1). The amidinium fragments are completely delocalized [C–N = 1.299(2) Å in **1**; 1.302(2) and 1.307(2) Å in **2**; 1.309(2) and 1.303(2) Å in **3**] and can be described as carrying a $\frac{1}{2}$ positive formal charge on the two nitrogens; the same delocalization occurs within the COO^- groups [C=O = 1.243(1) Å in **1**; 1.237(2) and 1.258(2) Å in **2**; 1.252(2) and 1.253(2) Å in **3**]. The two hydrogen bonds linking cation and anion are longer than it can be expected on the base of the classification of strong charge-assisted H-bonds (N···O distance range: 2.81–2.86 Å) because the remaining N–H hydrogens are involved in two other intermolecular H-bonds with the same oxygens belonging to different asymmetric units. The lack of H-bond acceptors with respect to H-bond donors gives rise to the formation of bifurcated H-bonds where each oxygen is the acceptor of two bonds, a very common situation for structures involving unsubstituted amidinium ions, as reported in the following discussion.

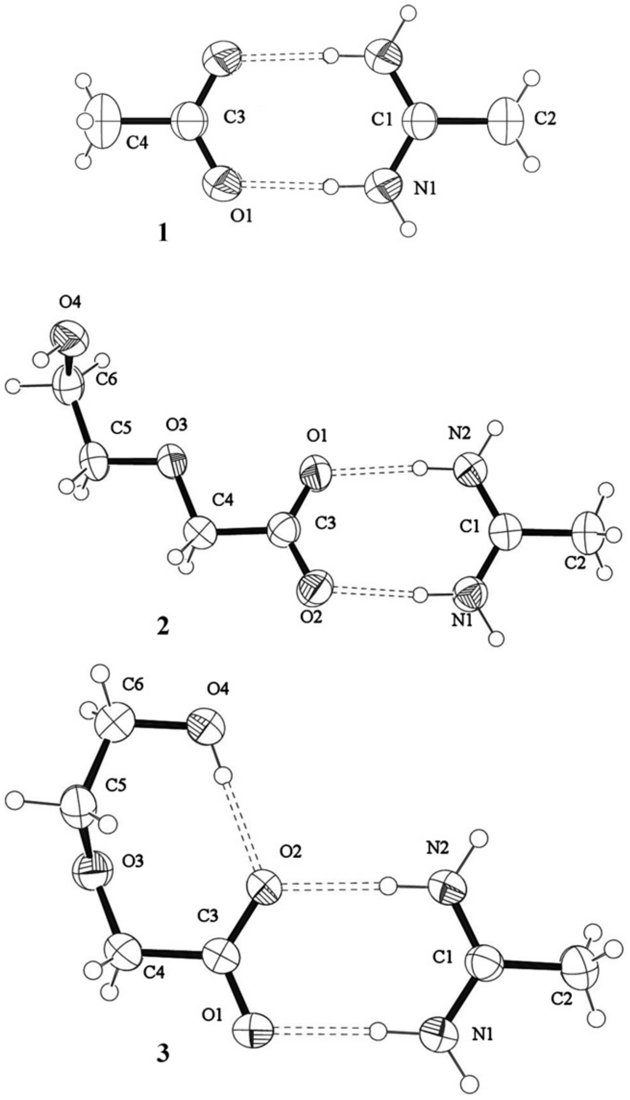

Fig. 1 ORTEP[11] views and atom numbering for compounds **1–3**. Thermal ellipsoids are drawn at the 40% probability level.

Table 1 Hydrogen bonding parameters (Å and degrees) with esd's in parentheses

D–H···A	D–H	D···A	H···A	D–H···A
1				
N1–Ha···O1	0.93(2)	2.820(2)	1.90(2)	172(2)
N1–Hb···O1^{i}	0.87(2)	2.796(2)	1.92(2)	176(2)
(i) $-x+1/2, -y, z-1/2$				
2				
N1–Ha···O1	0.92(2)	2.823(2)	1.91(2)	175(2)
N2–Hb···O2	0.91(2)	2.844(2)	1.93(2)	174(2)
O4–H···O2^{i}	0.90(3)	2.710(2)	1.81(3)	174(2)
N1–Hb···O1^{ii}	0.89(2)	2.856(2)	2.03(2)	153(2)
N2–Hd···O4^{iii}	0.94(2)	2.803(2)	1.87(2)	171(2)
(i) $-x, -y, 1-z$; (ii) $1/2-x, y-1/2, 1/2-z$ (iii) $x-1/2, -y-1/2, z-1/2$				
3				
N1–Ha···O1	0.94(2)	2.860(2)	1.92(3)	175(2)
N2–Hc···O2	0.91(2)	2.817(2)	1.91(3)	173(2)
O4–H···O2	0.81(3)	2.657(2)	1.85(3)	174(3)
N1–Hb···O4^{i}	0.90(2)	2.829(2)	1.95(2)	167(2)
N2–Hd···O1^{ii}	0.90(2)	2.815(2)	1.93(2)	166(2)
(i) $-x-1/2, y+1/2, -z-1/2$; (ii) $-x-1/2, y-1/2, -z-1/2$				

The asymmetric unit of compound **1** consists of a half of the complex with C1, C2, C3 and C4 atoms lying in a mirror plane. To analyze the hydrogen-bond pattern, shown in Fig. 2, it seemed useful to take advantage of the graph-set approach, originally proposed by Etter[12] and subsequently modified by Bernstein *et al.*.[13] It substantially reduces the description of a H-bond network to a combination of simple patterns, symbolized by a designator (*G*) with a subscript and a superscript giving the number of H-bond donors and acceptors, respectively. In parentheses the degree of the pattern, that is the number of atoms in the pattern, is reported. According to the graph-set approach, the first intermolecular N–H···O bond linking N1 and O1 atoms gives rise by symmetry to a planar $R_2^2(8)$ (R = ring) motif (the 'dimeric' synthon reported in Scheme 1), while the other one gives rise to a C(5) chain –N1–H···O1–C3–O1···H–N1– running along the *b* direction. The combination of these two motifs is at the origin (by symmetry) of a larger $R_6^4(16)$ ring (Fig. 2).

The (2-hydroxyethoxy)acetate in **2** (polymorphic form I) adopts a zig-zag fully elongated conformation. Its O4 atom acts both as a H-bond donor and acceptor, being linked head-to-tail to O2 to form a dimeric dianion that closes a $R_2^2(16)$ ring and receiving a H-bond from the N2 atom of the amidinium cation that links anions and cations in an infinite –C1–N2–H···O4–H···O2–C3–O1···H–N1– $C_3^3(10)$ chain running along the *a* direction. N1 and N2 atoms form, respectively,

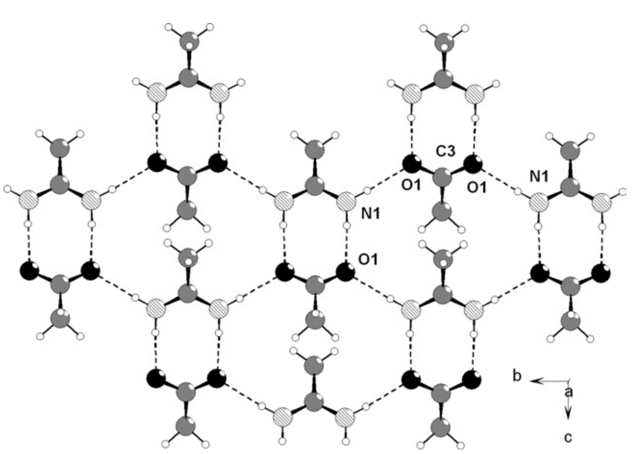

Fig. 2 Hydrogen bonding arrangement in the crystal of **1**.

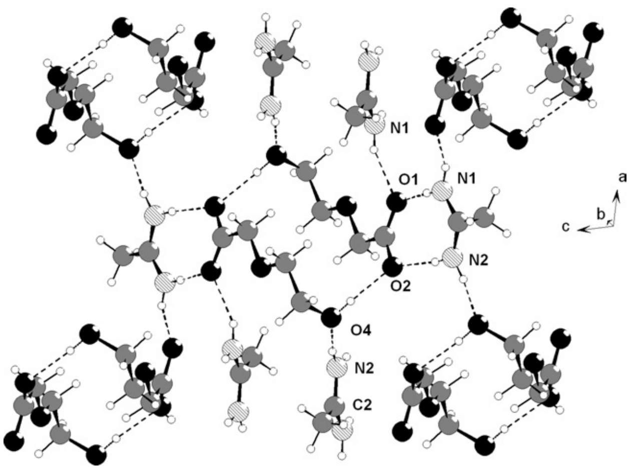

Fig. 3 Hydrogen bonding arrangement in the crystal of **2**.

H-bonds with O1 and O2 of the same asymmetric unit, giving rise to the usual $R_2^2(8)$ 'dimeric' ring. The resulting three-dimensional crystal arrangement is shown in Fig. 3.

The structure of **3** (polymorphic form II) differs from the previous one because of the different conformation adopted by the anion. It assumes a circular shape with the O4 atom forming an intramolecular H-bond with the O2 atom of the carboxylic group. Consequently, the crystal packing is completely different: two circular motifs are formed, S(8) (S being the designator for intramolecular bonds) for the anion and $R_2^2(8)$ (the 'dimeric' ring), and their combination gives rise to an infinite $C_3^3(10)$ chain –C3–O2···H–O4···H–N1–C1–N2–H···O1– and a larger $R_5^5(10)$ ring. The complete packing pattern is shown in Fig. 4.

Discussion

Packing mode analysis

A CSD search on acid-base complexes containing amidinium ion forming H-bonds with O^- oxygens has been performed. Ninety-nine structures have been retrieved, out of which 21 structures (6 solvated by water or ethanol) have cations carrying NH_2 unsubstituted groups and 78 are with NHR groups, the negatively charged oxygens belonging to different functional groups (carboxylic anions, carbonate, phosphate, nitrate, chlorate, *etc.*). For each structure H-bond parameters have been calculated and $N^+\cdots O^-$ distances are reported in Fig. 5 as separate histograms for the two classes of compounds. Mean N···O distances have been calculated to be 2.86(7) and 2.73(7) Å. The difference between the two values can be imputed mainly to the fact that in most cases of $R(NH_2)_2^+$ amidinium complexes each O^- oxygen accepts two H-bonds, forming bifurcated bonds, which are known to be weaker than the non-bifurcated ones.[14] The longest distances are associated with nitrate anions (5 structures), while the shortest with carboxylate anions, in agreement with the idea that the H-bond strength increases as the difference in pK_a between donor and acceptor atoms decreases.[15] Accordingly, N···O distances found in the present compounds lie in the range of 2.79–2.86 Å (see Table 1).

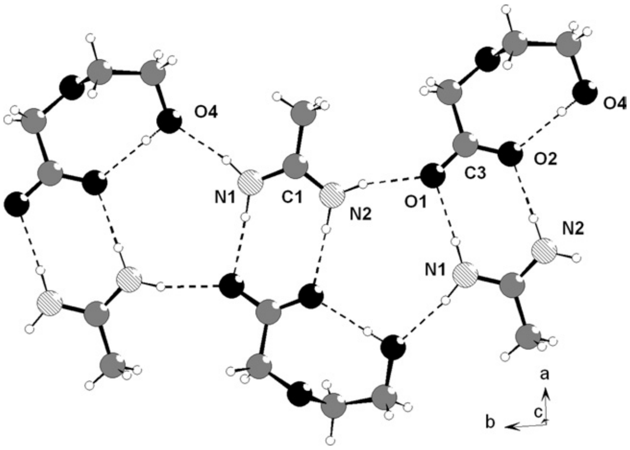

Fig. 4 Hydrogen bonding arrangement in the crystal of **3**.

A detailed analysis of the crystal packing architecture in the unsubstituted amidinium complexes revealed that the most frequent motif is the $R_2^2(8)$ cycle of Scheme 1 (20 cases), proving the robustness of this supramolecular synthon. The remaining structure not presenting such a structural motif, IBOKEP,[16] is a calixarene complex in which a great number of H-donor and acceptor atoms compete for H-bond formation. All the dimeric complexes are linked in the crystal lattice by H-bonds. In 5 cases co-crystallized solvent molecules (water or ethanol) are present and are always directly employed in the H-bond network, giving rise to very complicated packing patterns. Recognizable patterns are made by structures (4 cases, 5 hits) in which a single nitrate anion bridges three cations, forming a two-dimensional H-bond network, as displayed in Fig. 6 [the example is ECADIV[17] with a graph set characterized by $R_1^2(4)$ and $R_2^2(8)$ rings]. This pattern is reproduced in all the four cases, irrespective of the cation dimension (the R substituent of Scheme 1 varies from a methyl to a butyl group), and seems to be peculiar for the nitrate/amidinium couple. In only two structures, molecules are assembled into infinite ribbons (for example the packing of HEVSAC[18] in Fig. 7), while the remaining structures show packing patterns constituted by three dimensional H-bond networks, very difficult to predict '*a priori*'.

When the amidinium ion derives from secondary amines, the assembly of cations and anions becomes more predictable. The 'dimeric' motif is conserved in 26 cases, while infinite tapes and ribbons are easily formed when bifunctional moieties are used, as it was shown by Hosseini and coworkers in their structural studies on pyrimidinium ion–dicarboxylic acid complexes.[19] In Fig. 8 a typical example of such ribbons is reported for NEVYIW.[19a] It is evident from these works that a perfect match of the number of donors and acceptors (which is not achievable when 'primary' amidinium ions are used) results particularly important for the prediction of the crystal architecture. When the number of potential H-bond donors or acceptors or both increases, competition for H-bond formation results, leading to a greater variability in the possible packing patterns formed.

For comparison, a search was performed on the CSD, looking for neutral molecules or complexes containing an amidine (primary or secondary) and a carboxylic acid fragment. Only nineteen structures have been found showing N–H···O and O–H···N hydrogen bonds between the groups of interest; the mean values of the N–H···O distances are 2.84(9) and 2.99(9) Å for simple and bifurcated H-bonds, respectively. These values, as expected, are systematically longer than those reported above for charged complexes, which, being stabilized with respect to adducts formed by neutral moieties by the formation of strong CAHB bonds, are found in a greater number of structures.

Calculation results

The two polymorphs, as stated in the introduction, can be described as 'conformational polymorphs'[10] since the highly flexible (2-hydroxyethoxy)acetate molecule assumes completely different conformations in the two polymorphic modifications. It is reported (ref. 10 and references therein) that, in

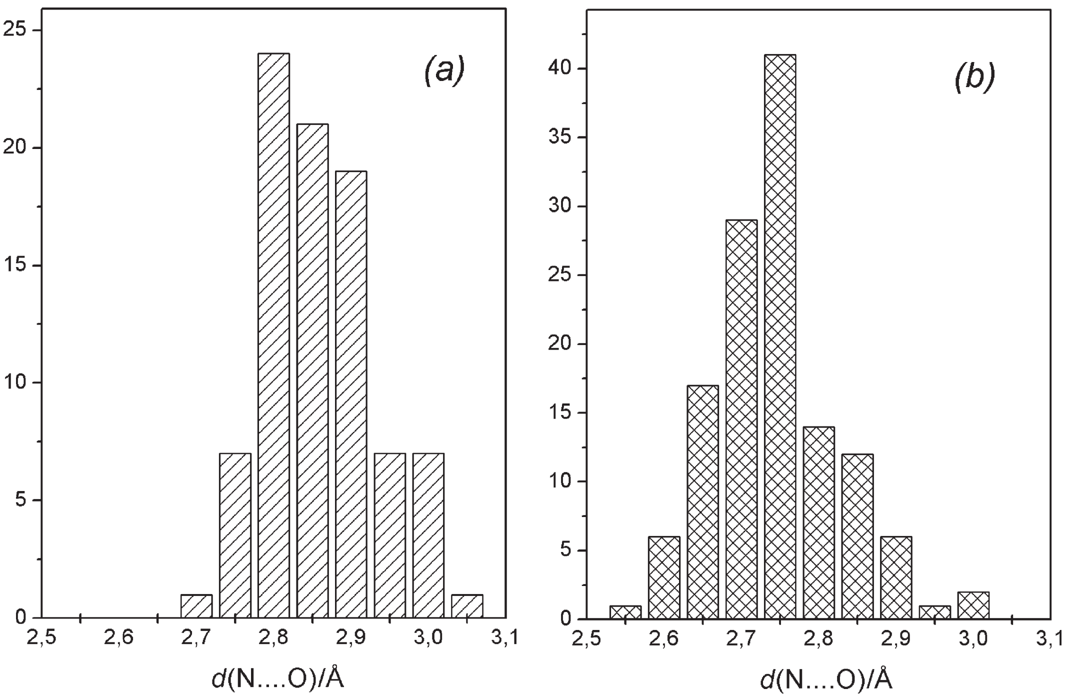

Fig. 5 Histograms of $N^{+}\cdots O^{-}$ contact distances in acid-base adducts containing (a) unsubstituted and (b) secondary amidinium cations.

general, the intramolecular strain energy difference among the conformers is around 1 kcal mol^{-1} and actually, in the present case, MM3 single point calculations indicate a torsional energy difference between the two crystallographic anion conformers of 1.4 kcal mol^{-1}. The cyclic form is of course stabilized '*in vacuum*' by intramolecular H-bond formation, as shown by DFT calculations at the B3LYP/6-31+G(d,p) level that have been carried out in order to obtain the equilibrium geometry and partial charges of the cation and anion, separately. The most stable conformation for the anion compares well with that found in polymorph II, as can easily be seen from Fig. 9. The calculated intramolecular H-bond $O\cdots O$ distance turns out to be 2.660 Å, in good agreement with that of 2.657(2) Å found in the crystal.

The evaluation of the crystal energy of the two polymorphs is not trivial as it must take into account many types of intermolecular forces: Coulombic, H-bonds, dispersion forces. Since from the quantum mechanical optimization only one anion conformer has been reproduced, the two different sets of Mulliken partial charges to be used in the crystal energy calculations have been evaluated on the fixed geometries found in the crystals by using DFT calculations at the B3LYP/6-31+G(d,p) level (see Experimental). The total energy of the two crystals, together with the contributions of the different intramolecular and intermolecular interaction terms, has been evaluated using the DREIDING force field.[20] The main contribution to the total energy is due to the Coulombic term, in agreement with the fact that the two moieties constituting the crystal are ionic; this contribution, however, is greatly overestimated (some −900 kcal mol^{-1} for both structures). Consequently, a discussion of the energy differences seems to be more informative: the total energies differ by 0.9 kcal mol^{-1}, polymorph I being the most stable, in line with the fact that the energy differences among polymorphs usually do not exceed 2–3 kcal mol^{-1} (see, for instance, ref. 21). The attractive contributions to the total energy of the H-bond term are strictly comparable at $\Delta E = 1.7$ kcal mol^{-1}, in agreement with the fact that, in spite of the different packing arrangement, the

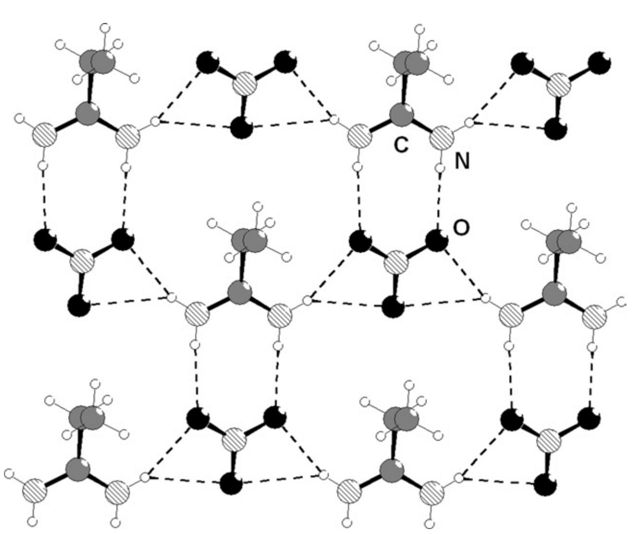

Fig. 6 Planar two-dimensional H-bond network in the crystal of ECADIV.[17]

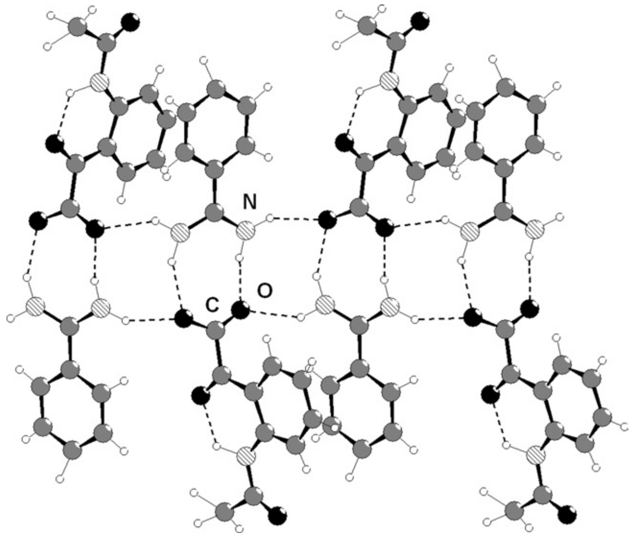

Fig. 7 Hydrogen-bonding arrangement forming infinite ribbons in the crystal of HEVSAC.[18]

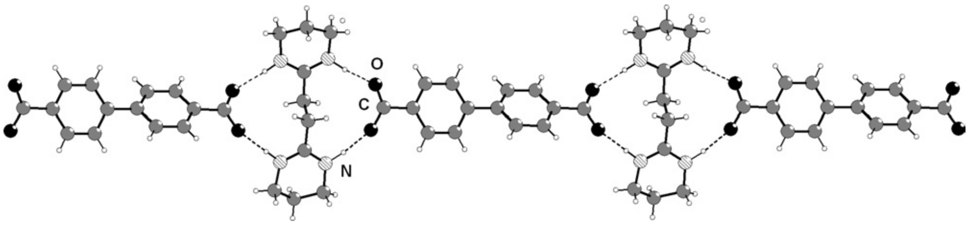

Fig. 8 Hydrogen-bonding arrangement forming infinite ribbons in the crystal of NEVYIW.[19a]

two polymorphs appear to be able to form the same number of H-bonds with almost identical structural characteristics (Table 1). The main differences concern the intramolecular terms (+23.7 and +46.8 kcal mol^{-1} in polymorphs I and II, respectively, with $\Delta E = 23.1$ kcal mol^{-1}) and the van der Waals interactions (+20.1 and +10.3 kcal mol^{-1} in polymorphs I and II, respectively, with $\Delta E = 9.8$ kcal mol^{-1}), as it could be expected in view of the fact that in the two polymorphs the flexible anion adopts completely different conformations. These results are a clear indication that, for an '*a priori*' predictability of crystal architectures, the relative rigidity of the molecular fragments constituting the co-crystal could play an important role, together with the matching of H-bond donor and acceptor functionalities.

Experimental

X-Ray crystallography

The complexes of amidinium–acetate (**1**) and amidinium–(2-hydroxyethoxy)acetate form I (**2**) and form II (**3**) were kindly provided by Prof. G. Baraldi (Department of Pharmaceutical Sciences, University of Ferrara). Suitable crystals for X-ray analysis were obtained by recrystallization from a mixture of chloroform and ethyl acetate (**1**), hot ethanol (**2**) and a mixture of chloroform and 2-propanol (**3**).

All X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer at room temperature using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) with a ϕ scan followed by a ω scan to fill the sphere. All intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods with the SIR97 program.[22] All structures were refined on F^2 by full-matrix least-squares methods with anisotropic non-H atoms while H atoms were found in the difference Fourier map and refined isotropically. All other calculations were accomplished using SHELX97[23] and PARST.[24] Selected crystal data are given in Table 2.†

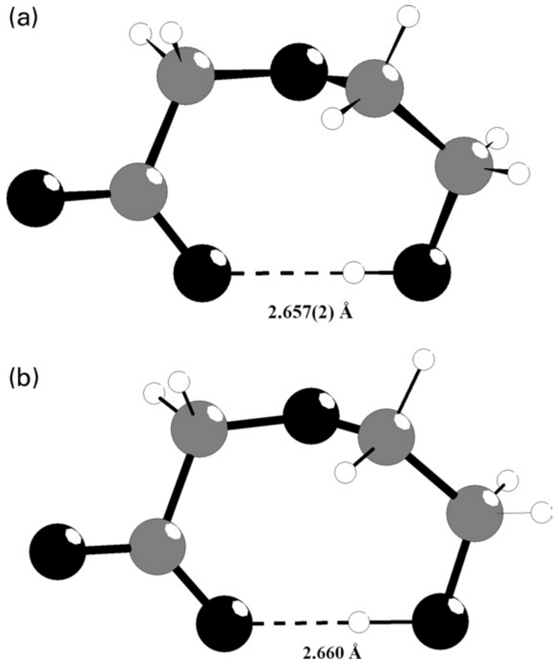

Fig. 9 Comparison between the conformation of (2-hydroxyethoxy)acetate anion (a) as found in polymorph II and (b) from DFT calculations.

CSD search

A total of 99 structures of amidinium ion–oxygenated anion (nitrate, carboxylate, phosphate, *etc.*) complexes and 19 structures of amidine–carboxylic acid adducts have been retrieved from the Cambridge Structural Database[9] (April 2003 version). Structures of low quality ($R > 10\%$), disordered or in which the positions of the H atoms have not been determined were excluded.

Table 2 Crystal data, data collection and refinement parameters for **1**–**3**

	1 Acetamidinium acetate	**2** Acetamidinium (2-hydroxy-ethoxy)acetate (Form I)	**3** Acetamidinium (2-hydroxy-ethoxy)acetate (Form II)
Formula	$[C_2H_3O_2]^-\cdot[C_2H_7N_2]^+$	$[C_4H_7O_4]^-\cdot[C_2H_7N_2]^+$	$[C_4H_7O_4]^-\cdot[C_2H_7N_2]^+$
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pnma*	$P2_1/n$	$P2_1/n$
a/Å	10.0507(4)	10.4295(4)	8.0426(3)
b/Å	9.2132(5)	7.7267(3)	11.4266(4)
c/Å	7.7953(6)	11.8844(6)	10.5017(5)
$\beta/°$	–	101.79(1)	108.089(2)
U/Å^3	721.84(7)	937.47(7)	917.51(6)
Z	4	4	4
T/K	296	296	296
D_x/Mg m^{-3}	1.087	1.262	1.290
μ/cm^{-1}	0.87	1.05	1.08
Unique reflections	919	2491	2094
R_{int}	0.038	0.032	0.029
Obs. reflections [$I > 2\sigma(I)$]	590	1544	1368
R (obs. reflns)	0.052	0.046	0.047
R_w (obs. reflns)	0.148	0.104	0.108

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† CCDC reference numbers 229598–229600. See http://www.rsc.org/suppdata/nj/b3/b314143h/ for crystallographic data in .cif or other electronic format.

Table 3 Calculated bond distances (Å) for the delocalized parts of the anion and cation

Cation		Anion	
C1–C2	1.498	C3–O1	1.266
C1–N1	1.325	C3–O2	1.253
C1–N2	1.323		

Calculations on amidinium–(2-hydroxyethoxy)acetate polymorphs

The lattice energies of the two polymorphs have been calculated using the DREIDING force field[20] in the CERIUS^2 system of programs[25], allowing a minimization of the molecular structures but keeping the unit cell parameters fixed. The Ewald method for periodic systems has been used[26] to evaluate non-bonded interactions (such as Coulombic interactions and attractive van der Waals interactions), imposing the re-calculation of the Ewald procedure parameters after each minimization iteration. Atoms were given Mulliken partial charges obtained from quantum mechanical calculations in the following way. Firstly, DFT calculations at the B3LYP/6-31+G(d,p) level using the Gaussian98 package[27] on the free cation and anion allowing a full optimization of the geometry have been performed. The calculated bond distances in the delocalized parts of the cation and anion fragments are reported in Table 3. The planar geometry of the amidinium cation is well reproduced by the calculations, while the optimized geometry of the anion turns out to be the circularly shaped one, due to the fact that *in vacuum* the molecule tends to form a intramolecular head-to-tail hydrogen bond as observed in polymorph II. For these reasons it seemed more appropriate to evaluate partial charges to be used in the subsequent crystal energy calculations by the DFT method at the B3LYP/6-31+G(d,p) level on the crystallographic geometries of the two different anionic conformations. During the calculation the position of the heavy atoms and the torsional angles involving hydroxyl hydrogens were kept fixed, allowing optimization of the other geometrical parameters (*i.e.*, bond lengths and angles involving H-atoms) due to the low accuracy of their crystallographically determined positions.

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