# Two-dimensional hydrogen-bonded networks in guanidinium hydrogen dicarboxylates

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***Received (in Montpellier, France) 12th October 2006, Accepted 19th December 2006***
***First published as an Advance Article on the web 12th January 2007***
**DOI: 10.1039/b614843c**

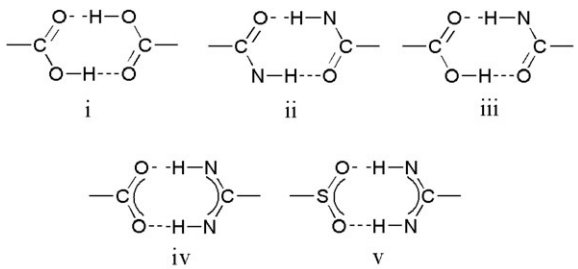
The crystal structures of three guanidinium hydrogen dicarboxylate systems are solved by X-ray diffraction methods and discussed with respect to similarities and dissimilarities of their hydrogen-bonded networks. The basic crystal chemical units in all of them are extended into ribbons, which are further organized in monolayers. However, the symmetry relations inside the layers vary from crystal to crystal and essentially depend upon the aliphatic spacer between the two carboxylic groups. Both the one- and the two-dimensional hydrogen-bonded networks in crystal **1** are polar and both are non-polar in crystal **2**, whereas in crystal **3** the ribbons are polar but the monolayers are non-polar.



## Introduction

During the last decade the synthetic and research efforts of chemists have moved from the traditional organic, inorganic, and organometallic chemistry to the problems of molecular assembly and crystal organization. The collective properties of well defined molecular assemblies have been addressed with respect to the structural relationships of individual components.[1] One of the fundamental principles of the supramolecular concept is the consideration that the intermolecular interactions act as supramolecular connections between the molecules in the same way as the covalent bonds connect the atoms in the molecule.[2] It is well appreciated that the ordered structural information for high level organization is deciphered in the molecules themselves.[1a,b] Nowadays this paradigm is particularly shifted towards controlling the periodic distribution of intermolecular (non-covalent) bonding and in this context the crystal is considered as a "supermolecule *par excellence*".[3] Variable approaches, targeted at high-dimensional arrangement of molecular/ionic building blocks with predictable final architecture, are being pursued by different research groups. With respect to its specific properties, such as directionality, selectivity and cooperativity, the hydrogen bond appears to be the most exploited interaction for structural organization and crystal design.

Guanidinium sulfonate systems are a good demonstration of reliable hydrogen-bonded networks issued by design. The equal number of separated hydrogen-bond donor and acceptor sites with matched geometry and stereoavailability allows the formation of persistent guanidinium sulfonate six-member modules (rosettes) periodically extended into saturated two-dimensional hydrogen-bonded networks (see Scheme 1). Noteworthy is that all three hydrogen-bonded motifs R2,2(8),[4a] used for generation of the network, correspond to synthon (v).[4b] The guanidinium monosulfonates display variable mono- and bilayer structures dependent upon the auxiliary R group,[5] whereas the disulfonates are merely forming clathrate compounds with form and size controllable filaments that depend upon the length and geometry of the R-spacer between the two sulfonate groups.[6]




The geometric and stereoelectronic complementarity of the carbamide and carboxylic groups also allow for predictable design of urea–dicarboxylic acid cocrystals. All three different basic units **UC**, **CUC** and **UCU**, formed upon varying the stoichiometric ratio of the components, use synthon (iii). The same synthon (iii) is applied also for the one-dimensional alignment of **UC** units into ribbons. However, the polymeric extensions of **CUC** and **UCU** units make use of an additional synthon: (i) in urea–bis(dicarboxylic acid) systems and (ii) in bis(urea)–dicarboxylic acids.[7] (Scheme 2)

The symmetry relations of the network depend explicitly on the internal molecular symmetry of the odd/even acids and the stoichiometry of the substrates. At room temperature, the even members of the α,ω-dicarboxylic series possess a center of inversion in the central C–C bond while the odd members, other than malonic acid, exhibit a two-fold rotational symmetry about the central carbon atom.[8] The dicarboxylic acids have been used to form various ionic or molecular cocrystal systems with imidazole, L-histidine, bisimidine, bent dipyridines, lutidines and many other molecules.[9]

The present work aims to study the structural organization in guanidinium dicarboxylate crystals. In particular, it focuses on revealing the rearrangement of the hydrogen-bonded networks resulting from modification of the recognition sites

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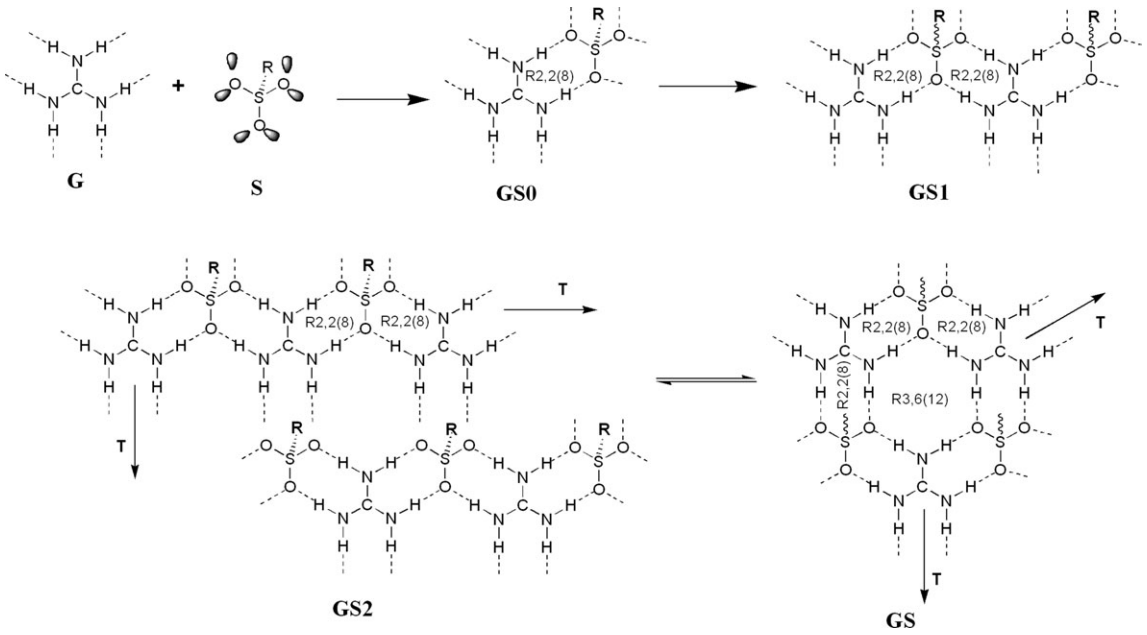
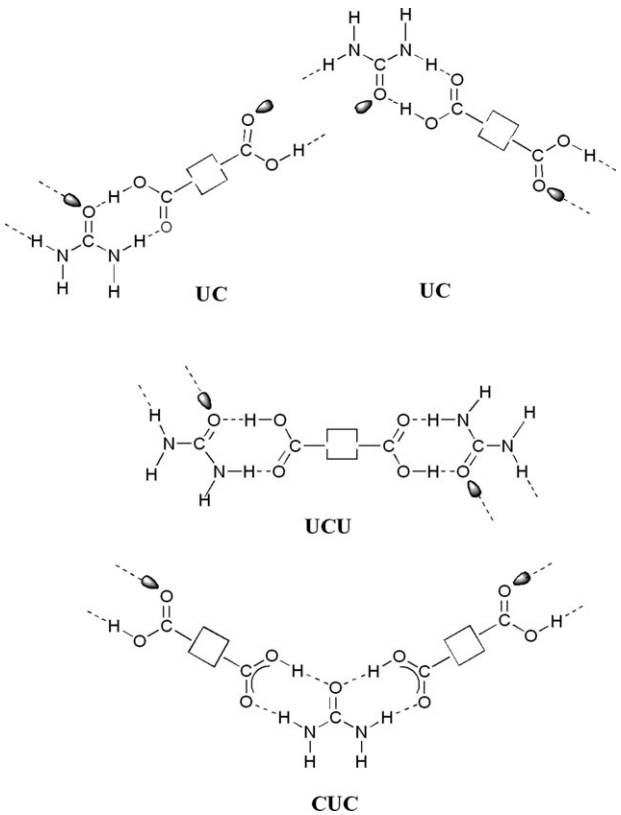



**Scheme 1**

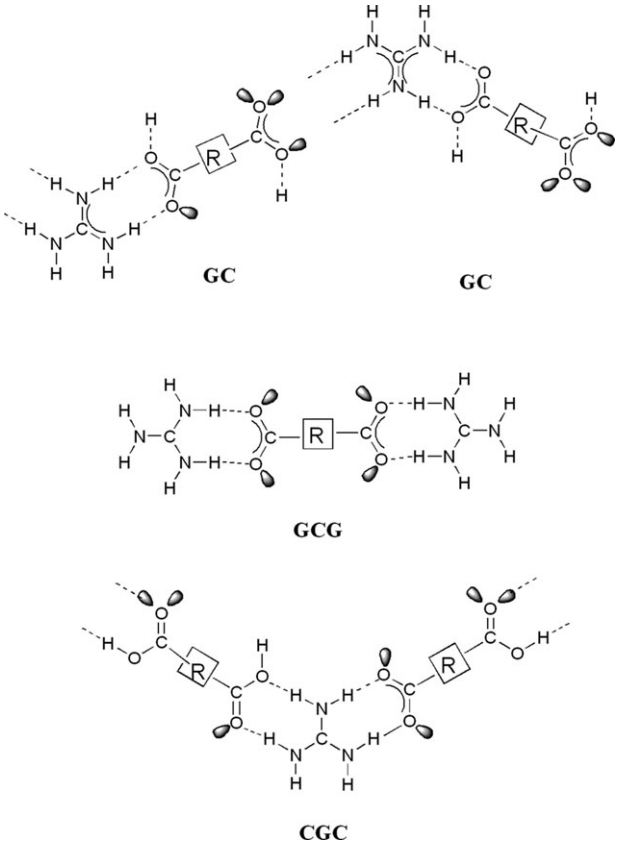



**Scheme 2**

compared to those in guanidinium sulfonates and/or urea–dicarboxylic acid systems. The guanidine molecule can be considered as an analogue of urea in which the carbonyl oxygen is replaced by the imino group =NH. It is among the strongest organic bases (p$K$ = 13.4) and easily protonates on the imino nitrogen in order to form a resonance stabilized ion with high symmetry (point group $D_{3h}$). Therefore, the hydrogen bond donor and acceptor sites in guanidinium carboxylates also become separated and hence the synthon (iv), applied for formation of the basic chemical unit **GC**, resembles the synthon (v), which was used in guanidinium sulfonates. However, the extension of the units in those two systems takes place in completely different manners (see Scheme 1 and Scheme 3). Due to acceptor deficiency of the carboxylate group, guanidinium monocarboxylates do not possess the potential for hydrogen-bond ribbon formation. On the other hand, the presence of two acceptor sites, spaced by an aromatic or aliphatic linker, allows for hydrogen-bond polymerization. It is easy to predict that the one-dimensional network in monoguanidinium dicarboxylates should be very similar to that in urea–dicarboxylic acids. In this view, it is reasonable to consider different guanidinium–dicarboxylate crystal chemical units, analogous to those in urea–dicarboxylic acid cocrystals,[7e] and to analyse their hydrogen-bond potential (compare Scheme 2 and Scheme 3).

Unlike **UCU** unit, the topology of the hydrogen-bond donors and acceptors in **GCG** unit does not permit the formation of polymeric ribbons. In this case we should note that whereas bis(urea)–dicarboxylic acid cocrystals are very readily formed,[7] a survey of the Cambridge Structural Data Base v.5.27 reveals only two records of bis(guanidinium) dicarboxylate crystals (FOVMEI and FOXPAJ).[10] However, full structural data are available only for bis(guanidinium) fumarate (FOVMEI). Indeed, only two of the guanidinium hydrogen atoms in this crystal are able to approach oxygen sites located on two different neighbouring units and the arrangement of the **GCG** units takes place in interdigitated manner without ribbon formation. Two water molecules, incorporated in the empty chambers generated between each four chemical units, serve as additional donor and acceptor sites in order to stabilize the structure.[11] On the other hand the




Scheme 3

availability of separate hydrogen-bond donor and acceptor sites, located on both ends of the monoguanidinium hydrogen dicarboxylate unit GC, favours the ribbon formation *via* synthon (iv). Only a few structures of monoguanidinium dicarboxylate crystals are reported in the literature, but they all are not adequate to our considerations.[12–14] The specific geometry of the acid[12] and the presence of additional functional groups[13] or solvate molecules[14] bring about the significant deformation of the hydrogen-bonded networks and they are more intricate as compared to those presented below. Hereafter we report the crystal structures of three monoguanidinium hydrogen dicarboxylate monocrystals and analyse the hydrogen-bonded networks in them.

## Experimental

### Materials and methods

All reagents and solvents used for synthesis are commercially available and used as received. The samples for FT IR spectra were prepared as Nujol mulls and measured on a Bruker IFS88 Spectrophotometer.

### Synthesis

Crystal **1** (guanidinium hydrogen succinate): 0.2389 g (2.023 mmol) of succinic acid and 0.1822 g (1.011 mmol) guanidinium carbonate ($Gn_2CO_3$) were dissolved in 70 ml methanol. The solution was stirred for 90 min in 30 °C and left to evaporate for 30 d. The dry precipitate was dissolved in 80 ml methanol, stirred for 80 min in 52 °C and left to recrystallize. Transparent, prism-like crystals of quality appropriate for X-ray measurements appeared in 3 d.

Crystal **2** (guanidinium hydrogen fumarate): 1.288 g (11.097 mmol) of fumaric acid and 1 g (5.550 mmol) of guanidinium carbonate were dissolved in 70 ml methanol. Additionally 50 ml $H_2O$ was added to the solution. Good quality crystals with a needle shape appeared in 25 d.

Crystal **3** (guanidinium hydrogen glutarate): 0.2413 g (1.826 mmol) of glutaric acid and 0.1645 g (0.913 mmol) of $Gn_2CO_3$ were dissolved in 30 ml methanol. The dry precipitate was recrystallized in methanol in order to get prism-like crystals.

### Single crystal X-ray diffraction studies

The X-ray diffraction data for compounds **1** and **3** were collected on a Kuma KM4 CCD four circle diffractometer[15] equipped with an Oxford Cryosystem Cooler using graphite monochromated Mo-K$\alpha$ radiation, $\lambda$ = 0.71073 Å. There was no evidence of crystal decay during the data collection. The structures were solved by direct methods using SHELXS and refined with SHELXL.[16] All measurements for crystal **2** were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-K$\alpha$ radiation and the structure was solved by direct methods with MITHRIL and DIRDIF.[17,18] The computer program PLATON was used for analysis and graphical presentation of the hydrogen bonding patterns.[19] The final refinements were performed by full-matrix least-square methods with anisotropic thermal parameters for all non-hydrogen atoms and based on w$F^2$ for crystals **1** and **3** and on w$F$ for crystal **2**. The hydrogen atoms in **1** and **3** were first observed in the difference electron density maps and then placed in calculated sites and included in the final refinement in the riding model approximation with fixed thermal factors. Further details for crystallographic data and structural analysis are listed in Table 1.†

## Results and discussion

### Crystal packing and hydrogen-bonded networks

The most important structural parameters in crystals **1–3**, compared with those of the starting materials are presented in Table 2. As expected, the bond distances of the spacer in **1–3** undergo only small changes as compared to those in the corresponding acids and the most notable changes are observed for the C–O bond relations of the end functional groups. The main point of our discussion will be focused on the solid state organization of the compounds with respect to the extended networks and the abundant hydrogen-bonded motifs. All three crystals display layer structures. The guanidinium cations and the monodeprotonated dicarboxylic anions are organized in flat layers *via* strong N–H···O and O–H···O hydrogen bonds established between them. The guanidinium ions link the acid residues using two similar R2,2(8) ring motifs (iv) in order to extend them into one-dimensional ribbons that are further hydrogen-bonded into a

† CCDC reference numbers 631518–631520. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614843c

**Table 1** Crystallographic data and structure refinement parameters

| | **GnHSuc 1** | **GnHFum 2** | **GnHGlut 3** |
|---|---|---|---|
| Chemical formula | $C_5H_{11}N_3O_4$ | $C_5H_9N_3O_4$ | $C_6H_{13}N_3O_4$ |
| Formula weight | 177.17 | 175.14 | 191.19 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P2_1/m$ | $P\bar{1}$ |
| Temperature/K | 293 | 297 | 100 |
| $a$/Å | 6.4910(10) | 3.696(3) | 5.2849(20) |
| $b$/Å | 18.388(4) | 18.824(5) | 8.501(3) |
| $c$/Å | 7.2300(10) | 5.496(2) | 10.466(4) |
| $\alpha$/° | 90.00 | 90.00 | 69.10(3) |
| $\beta$/° | 112.18(3) | 94.76(4) | 77.91(3) |
| $\gamma$/° | 90.00 | 90.00 | 89.42(3) |
| $V$/Å$^3$ | 799.1(2) | 381.1(4) | 428.4(3) |
| $Z$ | 4 | 2 | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.473 | 1.526 | 1.482 |
| $\mu$(MoK$_\alpha$)/mm$^{-1}$ | 0.127 | 0.132 | 0.124 |
| $F$(000) | 376.0 | 184.0 | 204.0 |
| Range of $h$, $k$, $l$ | −7 −6, ±21, −5 −8 | 0 −5, 25 −26, ±7 | ±6, ±11, ±13 |
| $\theta$ range/° | 3.24–24.99 | 2.8–29.95 | 3.89–27.99 |
| Reflections collected | 2852 | 2539 | 6197 |
| Independent reflections ($R_{int}$) | 1383 (0.1139) | 1153 (0.032) | 2040 (0.0215) |
| Reflections observed [$I > 2\sigma(I)$] | 1158 | 986 | 1848 |
| Refined parameters | 154 | 78 | 169 |
| $R_1$[a] | 0.060 | 0.053 | 0.0305 |
| w$R_2$ | 0.1716[b] | 0.067[c] | 0.0783[b] |
| All data $R_1$ | 0.0669 | | 0.0346 |
| All data w$R_2$ | 0.1796 | | 0.0809 |
| Goodness-of-fit | 1.075 | 2.17 | 1.075 |

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{\frac{1}{2}}$. [c] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{\frac{1}{2}}$.

**Table 2** Selected intermolecular bond lengths (Å )and bond angles (°)

| Bond | GnHSuc **1** | Succinic acid[8a] SUCACB08 | GnHFum **2** | Fumaric acid[8d] FUMAC01 | GnHGlut **3** | Glutaric acid[8a] GLURAC02 |
|---|---|---|---|---|---|---|
| C1–O1 | 1.307(2) | 1.323(6) | 1.298(1) | 1.291 | 1.304(1) | 1.320(1) |
| C1–O2 | 1.219(2) | 1.227(6) | 1.226(1) | 1.227 | 1.231(1) | 1.232(1) |
| **Δ(C–O)** | **0.087(2)** | **0.096(8)** | **0.072(1)** | **0.064** | **0.073(1)** | **0.088(1)** |
| C1–C2 | 1.509(2) | 1.502(6) | 1.492(1) | 1.490(5) | 1.513(1) | 1.450(1) |
| C2–C3 | 1.515(3) | 1.519(6) | 1.306(2) | 1.315(7) | 1.522(1) | 1.524(1) |
| C3–C4 | 1.514(2) | 1.502(6) | 1.492(1) | 1.490(5) | 1.522(1) | 1.524(1) |
| C4–C5 | | | | | 1.515(2) | 1.450(1) |
| C4–O3 | 1.284(2) | 1.323(6) | 1.298(1) | 1.291 | | 1.320(1) |
| C4–O4 | 1.241(2) | 1.227(6) | 1.226(11) | 1.227 | | 1.232(1) |
| C5–O3 | | | | | 1.298(1) | |
| C5–O4 | | | | | 1.235(1) | |
| **Δ(C–O)** | **0.043(3)** | **0.096(8)** | **0.072(1)** | **0.064** | **0.063(1)** | **0.088(1)** |

| | GnSuc | GnFum | GnGlu | $Gn_2CO_3$[22a] | GnCl[22b] |
|---|---|---|---|---|---|
| C10–N1 | 1.323(3) | 1.323(1) | 1.3320(14) | 1.321 | 1.325 |
| C10–N2 | 1.313(3) | 1.319(2) | 1.3296(13) | 1.318 | 1.316 |
| C10–N3 | 1.328(2) | 1.323(1) | 1.3327(14) | 1.347 | 1.325 |
| **Δ1** = (C10–N1)–(C10–N2) | 0.010(4) | 0.004(2) | 0.0024(19) | 0.003 | 0.009 |
| **Δ2** = (C10–N3)–(C10–N2) | 0.015(4) | 0.004(4) | 0.0031(19) | 0.026 | 0.009 |
| **Δ3** = (C10–N1)–(C10–N3) | 0.005(4) | 0 | 0.0007(20) | | |

[a] **Δ** = (C–O)–(C═O).

two-dimensional network. However, the symmetry relations inside the layers and between them are different in each of the crystals and essentially depend upon the covalent bond relations (even/odd number of C atoms) and, therefore, upon the orientation of the functional sites and the geometry of the monoanion. Fig. 1, Fig. 2 and Fig. 3 demonstrate the arrangement of the monolayers. The full information concerning hydrogen-bond interactions responsible for the organization is presented in Table 3.

### The crystalline network of guanidinium hydrogen succinate

A notable feature of this compound is that the guanidinium hydrogen succinate units are organized in polar monolayers

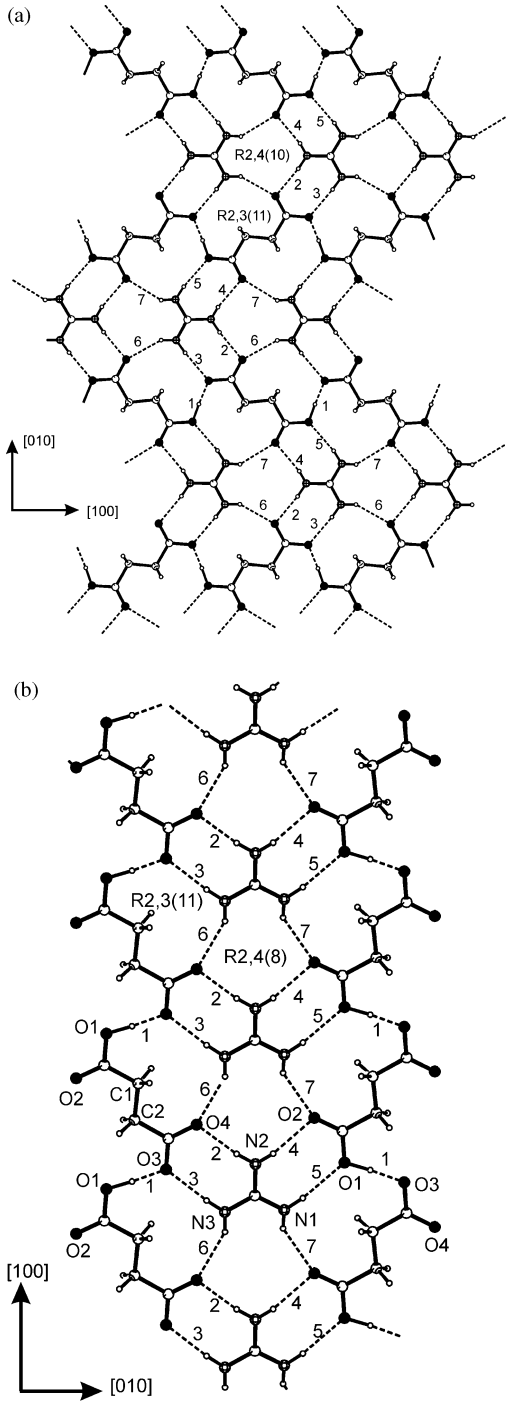



**Fig. 1** The two-dimensional hydrogen-bonded network in **1** can be described as: (a) parallel arrangement of translation related guanidinium hydrogen succinate ribbons; (b) arrangement of rotation related hydrogen succinate chains mediated (zipped) by guanidinium ions. In both instances the one-dimensional extensions are polar and therefore the monolayer is also polar. Note that the chains are perpendicular to the ribbons. The numbering of the hydrogen bonds is consistent with that in Table 3.

parallel to the (001) crystallographic plane. The guanidinium ion serves to link four different acid anions making use of five different hydrogen-bonded ring motifs. Two of them are the intra-ribbon motifs R2,2(8) (formed by two pairs of bonds 2,3 and 4,5). Transfer of one of the acid protons toward the imine nitrogen N2 of the guanidine molecule makes the end carboxylic groups distinguishable and more delocalized. The two C–O bonds of the deprotonated group become close in length (with a difference of 0.043(3) Å *versus* 0.096(8) Å in succinic acid). The carboxylic group on which the single proton is located also suffers some delocalization (with C–O and C═O bond lengths of 1.307(2) Å and 1.219(2) Å compared to 1.323(6) Å and 1.227(6) Å in the acid). The homomeric ring motif (synthon i) used in the acid chain is replaced by two heteromeric motifs (iv), formed between the guanidinium and the hydrogen succinate ions, and extending them into zig-zag ribbons along the *b*-direction. Generally the contact distances (hydrogen bonds assigned as 2 and 3) of the motif established between the guanidinium ion and the deprotonated end of the acid moiety are shorter than those on the opposite site (hydrogen bonds 4 and 5). The hydrogen bonds along the ribbons use explicitly the $N_{imine}$ hydrogen atoms and the $N_{amine}$ hydrogen atoms *syn*-oriented to them, and the *syn*-lone pairs of the oxygen atoms. The symmetry operator governing the 1D ribbon alignment is $2_1(y)$. The other two $N_{amine}$ hydrogen atoms, which are in the *anti*-orientation *versus* the C═$N_{imine}$ approach the *anti*-lone pairs of the oxygen atoms belonging to the neighbouring translation related ribbon in order to form two inter-ribbon hydrogen bonds (assigned as 6 and 7). A very short O–H···$O^-$ hydrogen bond (assigned as 1) is established between the carboxylic and carboxylate groups of adjacent ribbons. The *anti–anti* geometry of this interaction is very rare and worth attention since the carboxylic proton switches its orientation from *syn* to *anti* in order to approach the *anti*-lone pair of another hydroxyl oxygen. Hydrogen bonds 1, 3, 6 and 1, 5, 7 generate two different inter-ribbon motifs R2,3(11) and hydrogen bonds 2, 4, 6 and 7 generate another inter-ribbon motif R2,4(10). It is remarkable that only *syn*-lone pairs are exploited in the intra-ribbon hydrogen bonds while the *anti*-lone pairs in the inter-ribbon hydrogen bonds. So, the guanidinium sulfonate ribbons align in a parallel fashion and produce a polar monolayer. However, the layers pack with inversion relation and the overall 3D crystal structure is non-centrosymmetric.

### The crystalline network of guanidinium hydrogen fumarate

The organization of the monolayer in crystal **2** is similar to that in **1**. Each guanidinium ion hydrogen-bonds four acid residues and each fumarate anion is bonded to four guanidinium ions in order to form a monolayer parallel to the $(10\bar{1})$ crystallographic plane. The hydrogen-bond donors and acceptors display a *syn*-relation along the ribbons and an *anti*-relation between them. However, the symmetry relations of the two-dimensional network in **2** are completely different form those in **1**. Two symmetry elements ($\bar{1}$ imposed in the midline of the C═C bond and the mirror plane though the C═$N_{imine}$ bond) are operating along the ribbon. The bond conjugation along the aliphatic chain allows for resonance effects in **2** (*vs.* inductive effects in **1**) and consequently for equal electron delocalization of the end functional sites in the fumarate moiety. Therefore, the inherent molecular symmetry

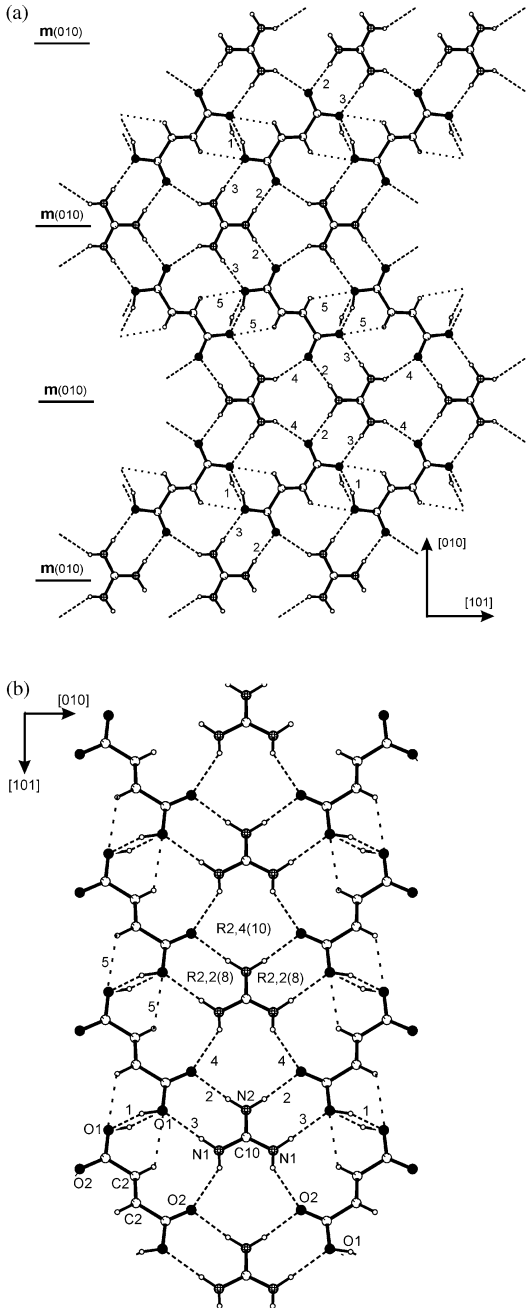



**Fig. 2** The two-dimensional hydrogen-bonded network in **2** can be described as: (a) parallel arrangement of inversion related guanidinium hydrogen fumarate ribbons; (b) arrangement of reflection related hydrogen fumarate chains mediated (zipped) by guanidinium ions. In both instances the one-dimensional extensions are non-polar and the monolayer is also non-polar. Note that the chains are perpendicular to the ribbons. The numbering of the hydrogen bonds is consistent with that in Table 3.

($\bar{1}$) is preserved also in the fumarate moiety. The second symmetry element ($m_{(010)}$ is a direct consequence of the identical guanidinium–fumarate interactions from both sides that generate identical R2,2(8) hydrogen-bond motifs. Thus, the one-dimensional ribbon alignment in **2** is dipolar. The alignment of the ribbons in the monolayer is antiparallel and takes place *via* $N_{amino}$–H···O(=C) (assigned as 4) and (C–)O–H–O(–C) (assigned as 1) hydrogen-bonds displaying *anti–anti* geometry. The fumarate proton, anti-positioned *vs.* the formal C=O bond, is shared (delocalized) between two equivalent (C–)O oxygen sites located on neighbouring inversion related ribbons. So the O–H–O bond (assigned as 1) established between the ribbons is symmetric. Similarly to **1**, the geometry of this bond is *anti–anti*, but the O···O distance in **2** shorter than that in **1**. Only three different hydrogen-bonded motifs are generated in this crystal. One of them, R2,2(8) (*via* hydrogen bonds 2 and 3), is intra-ribbon and the other two, R2,3(11) (*via* 1, 3 and 4) and R2,4(10) (*via* 2 and 4), are inter-ribbon motifs. The monolayers in the crystal stack in a parallel manner one over the other along the [10$\bar{1}$] crystallographic direction.

### The crystalline network of guanidinium hydrogen glutarate

Differences in the molecular geometry and inherent symmetry of the odd- and even-numbered series of α,ω-dicarboxylic acids are the reason for the different recognition events and crystal packing patterns and therefore for the different trends in the melting point alternations and the solid state densities observed in both series.[8a,b] The basic crystal units in **3** also form hydrogen-bonded ribbons along the [1$\bar{1}$1] direction, which are further arranged in monolayers. However the organization of the monolayer in **3** is quite different from that in **1** and **2**. Both carbonyl groups in glutarate monoanion are *Z*-oriented *versus* the aliphatic spacer compared to the *E*-orientation in **1** and **2**. This dramatically changes the recognition abilities of the glutarate moiety and the geometry of interactions with the guanidinium ion, which has significant consequences for the ribbon formation and the monolayer alignment. As in the former two crystals each ion is closely surrounded by four counter ions. However, only three glutarate moieties are hydrogen-bond accessible for a single guanidinium ion and *vice versa*, each glutarate anion is hydrogen-bond approached by only three cations, which issues into completely different connectivity patterns in this crystal. Two different pairs of hydrogen bonds (2,7, and 3,6) are used in the formation of the R2,2(8) motifs along the ribbon, which contributes to the polarity of the one-dimensional alignment. On the other hand, the ribbons in **3** display different recognition properties from both sides. Only (C=)O and N–H sites are available from one side of the ribbon, while the (C–)O sites are arranged from the opposite side. So, the two guanidinium hydrogens not used in the ribbon extension are able to approach the (C=)O *anti*-lone pairs of the neighbouring inversion related ribbon *via* two hydrogen bonds (4 and 5), thus linking the similar sides in order to form a 'double ribbon' (Fig. 3). Two R2,4(8) and one R2,2(12) motifs are generated in there. The acidic protons of the glutarate monoanions are arranged from outer side of the 'double ribbons' and are shared between identical (C–)$O_{anti}$ sites that belong to neighbouring 'double ribbons'. The short and symmetric O–H–O bond, with *anti–anti* geometry, established between the inversion related 'double ribbons' links them into a monolayer (see Fig. 3a). Two weak hydrogen bonds (assigned 8 and 9), established between the $C_{\alpha}$–H and (C–)O sites, are additionally stabilizing the monolayer. The inter-ribbons linking

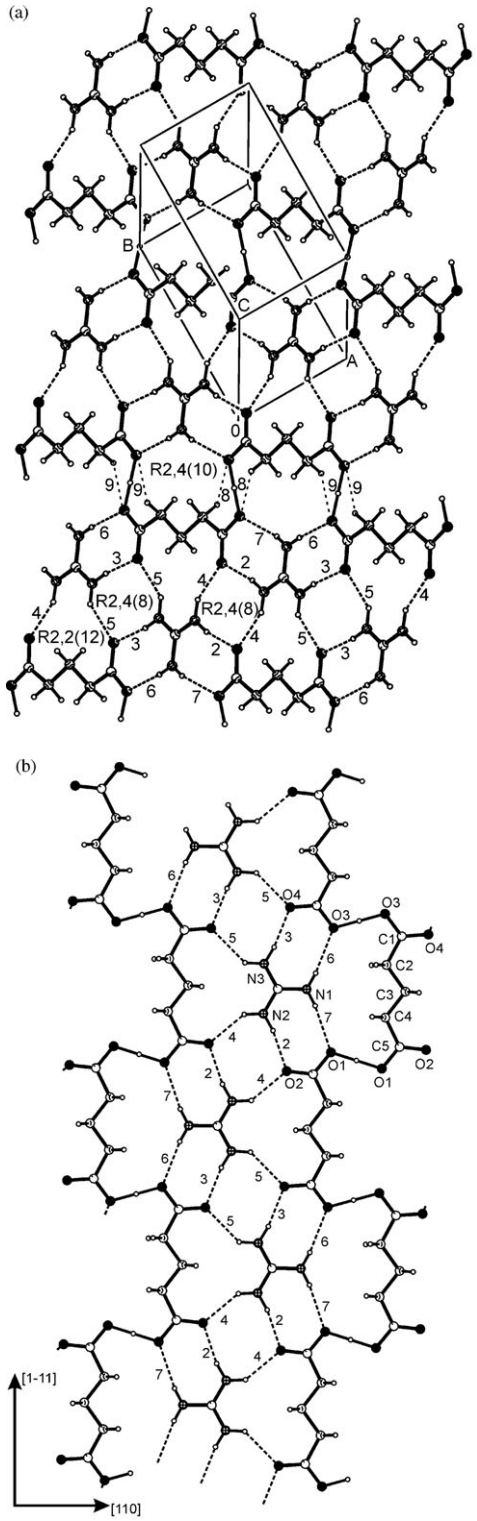



**Fig. 3** The two-dimensional hydrogen-bonded network in **3** can be described as: (a) parallel arrangement of inversion related guanidinium hydrogen glutarate ribbons; (b) parallel arrangement of translation related hydrogen glutarate chains zipped by guanidinium ions. Note that, unlike crystal **1** and **2** the chains in **3** are running along the ribbons. The arrangement of the chemical units along the ribbons is head to tail, whereas the anionic chains are centrosymmetric and therefore the monolayer in **3** is also non-polar.

motifs in **3** are different from those in **1** and **2**. One R2,2(12) (formed by 4 and 5) and two different centrosymmetric R2,4(8) motifs are generated inside the 'double ribbons'. Another R4,4(14) motif is generated between them using the hydrogen bonds assigned as 1, 6 and 7. Balanced electrostatic effects suffered by the guanidinium ion contribute for the entire delocalization of its electron system. The length differences of the three guanidinium C–N bonds became statistically insignificant (at $3\sigma$ level of the standard deviations) and there is no differentiation between C–$N_{amino}$ and C═$N_{imino}$ bonds as well as between *syn* and *anti*-positions of the proton donors in **3**. The monolayers in **3** are parallel to the ($\bar{1}12$) crystallographic plane and arranged on top of each other.

### Hydrogen-bond polymerization of the dicarboxylate monoanions

An alternative way to describe the monolayer organization in these crystals is to consider them as built up from polymeric hydrogen dicarboxylate chains that are zipped by the guanidinium ions. The monoanionic chains run along the [100] crystallographic direction in **1**, along [101] in **2** and along [$1\bar{1}1$] in **3**. The symmetry relations along the chains depend upon the parallel/antiparallel orientation of the end functional groups, *i.e.* upon the symmetry of the acid backbone. The different orientation of the two end C–O bonds (*E* for even-numbered and *Z* for odd-numbered spacers) essentially changes the anion–cation hydrogen-bond interrelations along the anionic chains. The guanidinium ions in **1** and **2** are arranged from both side of the anionic chains and serve to zipper them *via* two R2,2(8) motifs in order to form a 2D hydrogen-bonded network (Fig. 1b, Fig 2b and Fig 3b). So, the guanidinium–dicarboxylate ribbons are developed in a direction perpendicular to that of the anionic chains. However, in crystal **3** the anionic chains are running parallel to the guanidinium glutarate ribbons, which issues into different recognition patterns between the ribbons (Fig. 3b).

It should be noted that, unlike the catameric *syn–anti* (C–)O–H···O(═C) bond donated from the carboxylic hydrogen atom (in *syn*-position *vs.* C═O) toward the *anti*-lone pair of adjacent carbonyl oxygen, the O–H···$O^-$ bond in crystals **1–3** is formed between the oxygen atoms of formally single C–O bonds and the proton is *anti*-positioned *vs.* both C═O bonds (see Fig. 1b, Fig 2b and Fig 3b). This kind of *anti–anti* O–H···$O^-$ hydrogen bond is very rare indeed, and present only when there is an additional stabilization from other (ionic) interactions.[20] A search in CSD v. 5.27 reveals 117 hits of *syn–anti* and only five *anti–anti* O–H···$O^-$ carboxylic–carboxylate hydrogen bonds (ICEKAD, MANPIB, MAHPOH, VPTMEV, XIVBIN).

The proton behaviour (dynamics) in very short hydrogen bonds is sensitive even to tiny changes in the surroundings. On the other hand the symmetry of the O–H···$O^-$ bond essentially dictates the relations along the anionic chain and can effectively disturb the resonance structure of the guanidinium ion. So, the operator of translation is governing the 1D alignment of the succinate monoanions into polar chains with a hydrogen-bond proton localized by one of the carboxylic groups. In crystals **2** and **3** the anionic arrangement

**Table 3** Hydrogen-bond geometries and hydrogen-bonded patterns in crystals **1**–**3**

| No. | Hydrogen-bond interactions | D–H/Å | H···A/Å | D···A /Å | ∠DHA/° | Symmetry code | H. B. motif |
|---|---|---|---|---|---|---|---|
| | **GnHSuc 1** | | | | | | |
| 1 | O1–H1···O3 | 1.06(3) | 1.43(3) | 2.481(2) | 177(3) | $1 + x, y, z$ | C(7) |
| | Molecular ribbons along *b*-axis | | | | Screw relation along the ribbons | | |
| 2 | N2–H22N···O4 | 0.89(3) | 2.00(3) | 2.885(2) | 172(3) | $1 + x, y, z$ | R2,2(8) |
| 3 | N3–H13N···O3 | 0.87(3) | 2.05(3) | 2.915(2) | 175(2) | $1+, y, z$ | |
| 4 | N2–H12N···O2 | 0.80(3) | 2.11(3) | 2.900(2) | 170(3) | $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ | R2,2(8) |
| 5 | N1–H21N···O1 | 0.86(3) | 2.14(3) | 2.995(2) | 172(3) | $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ | |
| | Molecular monolayers (001) | | | | Translation relation between the ribbons | | |
| 6 | N3–H23N···O4 | 0.84(3) | 2.25(3) | 3.000(2) | 150(2) | $x, y, z$ | |
| 7 | N1–H11N···O2 | 0.81(3) | 2.32(3) | 3.025(3) | 146(2) | $-x, \frac{1}{2} + y, \frac{3}{2} - z$ | |
| | **GnHFum 2** | | | | | | |
| 1 | O1–H1···O1 | 0.91(4) | 1.58(4) | 2.464(2) | 161(4) | $2 - x, -y, 2 - z$ | C(7) |
| | Molecular ribbons along *b*-axis with alternating symmetry elements: $\bar{1}$ on the midline of C2═C2 and $m(\perp b)$ through C10═N2 bond | | | | | | |
| 2 | N2–H12N···O2 | 0.907(2) | 1.967(2) | 2.871(3) | 174.3(2) | $x, y, z$ | R2,2(8) |
| 3 | N1–H21N···O1 | 0.91(2) | 2.08(2) | 2.987(3) | 177(2) | $x, y, z$ | |
| | Molecular layers (101) | | | | Translation relation between the ribbons | | |
| 4 | N1–H11N···O2 | 0.86(3) | 2.27(2) | 3.006(3) | 145.2(2) | $1 + x, y, 1 + z$ | |
| 5 | C2–H2C···O1 | 0.95(2) | 2.53(2) | 3.203(3) | 128.1(2) | $2 - x, -y, 2 - z$ | R2,2(8) |
| | **GnHGlut 3** | | | | | | |
| 1a | O1–H1···O1 | 1.24 | 1.24 | 2.476(2) | 180 | $1 - x, 1 - y, 1 - z$ | C(8) |
| 1b | O3–H3···O3 | 1.24 | 1.24 | 2.476(2) | 180 | $-x, 2 - y, -z$ | C(8) |
| | Molecular ribbons along $[1\bar{1}1]$ | | | | Translation relation along the ribbons | | |
| 2 | N2–H12N···O2 | 0.903(2) | 1.990(2) | 2.881(2) | 168.9(2) | $x, y, z$ | R2,2(8) |
| 3 | N1–H21N···O1 | 0.870(2) | 2.292(2) | 3.143(2) | 169(2) | $x, y, z$ | |
| 4 | N3–H23N···O4 | 0.900(2) | 1.997(2) | 2.888(2) | 170.7(2) | $1 + x, -1 + y, 1 + z$ | R2,2(8) |
| 5 | N1–H11N···O3 | 0.853(2) | 2.268(2) | 3.114(2) | 171.4(2) | $1 + x, -1 + y, 1 + z$ | |
| | Molecular monolayers ($\bar{1}12$) | | | | Inversion relation between the ribbons | | |
| 6 | N2–H22N···O2 | 0.892(2) | 2.131(2) | 2.887(2) | 142.1(1) | $-x, -y, 1 - z$ | R2,2(12) |
| 7 | N3–H13N···O4 | 0.892(2) | 2.238(2) | 2.956(2) | 137.2(1) | $-x, -y, 1 - z$ | |
| 8 | C2–H12···O1 | 0.978(2) | 2.573(1) | 3.001(2) | 106.5(8) | $1 - x, 1 - y, 1 - z$ | R2,2(8) |
| 9 | C4–H24···O3 | 0.980(2) | 2.590(2) | 2.994(2) | 104.8(1) | $-x, 2 - y, -z$ | R2,2(8) |



into non-polar chains is governed by the operator of inversion and the hydrogen-bond proton is distributed between the oxygen sites of neighbouring anions. However, neither diffraction nor spectroscopic methods are able to authoritatively distinguish between a single minimum and a low-barrier double minimum potential in a case of very short and symmetric OHO hydrogen bonds.

## Conclusions

This study has demonstrated the organizational potential of guanidinium ion to form two-dimensional hydrogen-bonded networks with dicarboxylic acids. The transfer of one of the acid protons toward the imino nitrogen atom of guanidine results in separation of the hydrogen bond donor and acceptor sites in monoguanidinium hydrogen dicarboxylates and makes the **GC** synthon (iv) resemble the **GS** synthon (v), rather than the **UC** synthon (iii). Nevertheless, the one-dimensional hydrogen-bonded networks in these crystals are very similar to those in urea–dicarboxylic systems and completely differ from those in guanidinium sulfonates. The resonance stabilization of the guanidinium ion allows for symmetric electron delocalization of the end functional groups of the monoanion with a resultant sharing of the single acidic proton. On the other hand the inherent molecular symmetry of the dicarboxylic acid is determining the anion–cation arrangement in the monolayer. Therefore the symmetry relations along the ribbons, as well as between them, are different in each of the crystals. The ribbon alignment is polar in crystals **1** and **3** and non-polar in crystal **2**. The inter-ribbon relations in **2** and **3** are antiparallel and the monolayers in them are nonpolar. Only crystal **1** displays a polar organization of the monolayers. Variable layered structures assembled with strong O–H···O and N–H···O, or weak C–H···O hydrogen bonds, demonstrate polar two-dimensional motifs.[9a,21] However, the factors that can promote a non-centrosymmetric crystallization with implications in material science are still not well understood. So the task of controlling parallel stacking of polar domains in 3D crystals continues to be a challenge for crystal engineers.

## Acknowledgements

Financial support from KBN (grant 4 T09A 121 24) and Wrocław University of Technology are gratefully appreciated.

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