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# Three-Dimensional Self-Assembly Supramolecular Structure of Hydrogen Bonded Melaminium Citrate

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The melaminium dihydrogencitrate, $(C_3H_7N_6)(HOOC–CH_2–C(OH)(COOH)–CH_2–COO)$, crystallizes from water solution at room temperature in the $P2_1/c$ space group of the monoclinic system with the lattice parameters of $a$ = 5.531(1), $b$ = 20.869(4), $c$ = 11.282(2) Å and $\beta$ = 99.96(3)° and $Z$ = 4. The crystals are built up from singly protonated at the one N-ring atom melaminium cations that interact in a near linear fashion through a pair of N–H···N hydrogen bonds to form the centrosymmetric dimeric structure. The dihydrogencitrate(–) anions interact in the head-to-tail fashion *via* the terminal dissociated ($COO^-$) and non-dissociated (COOH) carboxyl groups to form O–H···O hydrogen bonded zigzag infinite chains. The hydroxyl group of dihydrogencitrate(–) ions is involved into O–H···O hydrogen bonds that linked together the dihydrogencitrate(–) chains into two-dimensional network. The centrosymmetric dimers of melaminium moieties interact with the sheets of dihydrogencitrate(–) to form the three-dimensional hydrogen bonded network. The conformation of the dihydrogencitrate(–) ion in the crystal is compared with the conformation in the gas-phase obtained by the *ab-initio* molecular orbital calculation.

**Key words**: melaminium, citrate, crystal structure, self-assembling, conformation, hydrogen bond

Self-assembling of small molecules into noncovalent supramolecular arrays is currently extensively used in the crystal engineering and supramolecular chemistry and technology [1,2]. The hydrogen bonding is the main key for organization the elements as well as the force responsible for the stability of well-defined supramolecular architectures [3–6]. The N–H···N, N–H···O and O–H···O hydrogen bonds have been used in the design of a number and different supramolecular structures as ribbons, rosettes, layers, tubes, rods, spheres and sheets [7–12]. Some supramolecular motifs of hydrogen bonding patterns of symmetric and translational repetitive occurrence are important in the crystal and chemical engineering [13]. The usually weak C–H···N and C–H···O hydrogen bonds also play a significant role in the formation and stabilization of supramolecular architectures, especially in the biological systems [14]. The formation of a noncovalent association of proteins and ligands, formation of a pho-

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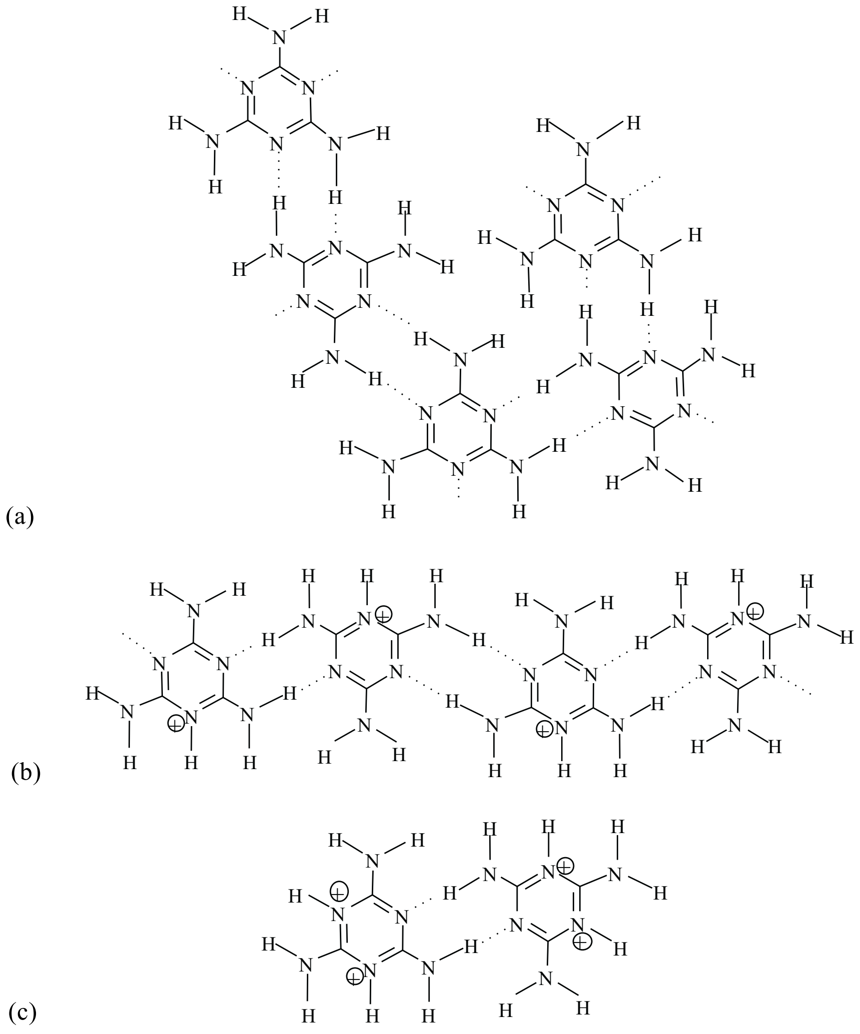
spholipid bilayer, interaction of a transcription factor with DNA, and folding of a tRNA into its three-dimensional conformation are examples of processes that depend on noncovalent interactions and organizations [14].

Melamine and its organic and inorganic complexes or salts can develop supramolecular structures *via* multiple hydrogen bonds through self-assembly of components, containing complementary arrays of hydrogen bonding sites. Melamine forms in the solid-state a two-dimensional network (Scheme 1a) [15]. Protonation of the triazine ring decreases the number of active sites and leads to decreasing of dimensionality of the arrangement, for example singly protonated melaminium cations form one-dimensional hydrogen bonded chain (Scheme 1b), while the doubly protonated melaminium cations form only a dimeric structure (Scheme 1c).

Scheme 1



Our interest in the melamine and its complexes or salts arises from the possibility to obtain new materials for non-linear optics. The crystals of melaminium selenate with the non-centrosymmetric space group are optically active and generate the SHG (second harmonic generation) with *ca.* 40% efficiency [16]. Another non-centrosymmetric crystal of melaminium phosphate [17] may be also used as material with non-linear properties. A number of other hydrogen-bonded superstructures of new melaminium salts have been recently characterized [18–26]. The present investigation has been carried out in order to study the conformation and the pattern of the hydrogen bonding system present in the crystal of melaminium citrate. In addition, the geometries of both oppositely charged parts, *i.e.* the singly protonated melaminium cation and the citrate anion, are compared with the *ab-initio* molecular orbital calculation.

## EXPERIMENTAL

***Preparation.*** Melaminium citrate was prepared by mixing a hot water solution of melamine (obtained from Aldrich) with hot water solution of citric acid (Aldrich) in a 1:1 molar ratio. The mixture was cooled slowly and kept at room temperature. After several days colourless crystals were obtained.

***X-ray crystallography.*** A colourless single crystal of melaminium citrate with the dimensions of 0.30×0.28×0.25 mm was used for data collection on a four-circle KUMA KM-4 diffractometer equipped with two-dimensional area CCD detector. The monochromatized MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å) and $\omega$-scan technique with $\Delta\omega = 0.75°$ for one image were used for data collection. The 960 images for six different runs covering over 95% of the Ewald sphere were performed. The lattice cell parameters were refined on the basis of all collected reflections with $F^2 > 2\sigma(F^2)$. One image was monitored as a standard after every 40 images for control the stability of the crystal. Integration of the intensities was performed using a KUMA KM-4 CCD software [27]. The face-indexed analytical absorption correction was calculated using *SHELXTL* program [28]. The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms using *SHELXL-97* program [29]. The hydrogen atoms were located from the difference Fourier maps and their positional parameters were refined. The final difference Fourier synthesis showed no peaks of chemical significance. The final agreement factors and details of the data collections were collected in Table 1.

**Table 1.** Crystallographic data for melaminium dihydrogencitrate, details for data collection and refinement parameters.

| | |
|---|---|
| Formula | $C_9H_{14}N_6O_7$ |
| Mol. wt. | 318.26 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Unit cell dimensions $a$, $b$, $c$, (Å) | 5.310(1), 20.869(4), 11.282(2) |
| $\beta$ (°) | 99.96(3) |
| Volume, $V$ (Å$^3$) | 1282.6(4) |
| $Z$ | 4 |
| $F$(000) | 664 |
| $D_{calc}$ (g/cm$^3$) | 1.648 |
| $D_{obs}$ measured, flotation (g/cm$^3$) | 1.645 |
| Radiation, MoK$\alpha$, (Å) | $\lambda$ = 0.71073 |
| 2$\theta$ max. | 57.8 |
| Refls collected | 11981 |
| Independent refls | 3238, ($R_{int}$ = 0.0131) |
| Observed refls | 2740 |

Table 1 (continuation)

| | |
|---|---|
| Absorption coefficient, $\mu$, (mm$^{-1}$) | 0.143 |
| Correction | Lorentz, polarization, face-indexed analytical absorption, $T_{\max} = 0.9652$, $T_{\min.} = 0.9585$ |
| Refinement on $F^2$ | |
| $R(F^2 > 2\sigma(F^2))$[a] | 0.0301 |
| $wR$ ($F^2$ all reflections)[b] | 0.0754 |
| Goodness-of-fit, $S$ | 1.0013 |
| Residual electron density, e Å$^{-3}$ | +0.245, –0.183 |

[a] $R = \Sigma\,||F_o| - ||F_c|/\Sigma F_o$.
[b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w F_o^4\}^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0384P)^2 + 0.3510P]$, where $P = (F_o^2 + 2F_c^2)/3$.

***Theoretical calculations***. *Ab-initio* molecular orbital calculations were performed with the Gaussian94 program package [30]. Full optimization was carried out with the B3LYP/6-31G(d,p) basis sets functions, starting from the X-ray geometry. The DFT methods that include the electron correlation effects have been used to predict the geometry of both ionic parts of the compound. As convergence critetions the threshold limits of 0.00025 and 0.0012 a.u. were applied for the maximum force and for the displacement, respectively. The calculations were performed on the isolated and non-interacting ions of singly protonated melaminium residue and for the one dissociated citrate anion.

## RESULTS AND DISCUSSION

The molecular structure of melaminium dihydrogencitrate obtained by the X-ray single crystal analysis with the labelling scheme is shown in Figure 1. The X-ray experimental geometrical parameters are given in Table 3, which also comprises the *ab-initio* full-optimized parameters calculated at the B3LYP/6-31G(d,p) level. The molecular orbital calculations were performed separate for the melaminium cation, $(C_3H_7N_6)^+$, and separate for the dihydrogen citrate anion $(HOOC–CH_2–C(OH)(COOH)–CH_2–COO^-)$. The crystals of the title compound are built up from the singly protonated at the ring N atom melaminium cations, $(C_3H_7N_6)^+$, and singly dissociated citrate anions $(HOOC–CH_2–C(OH)(COOH)–CH_2–COO^-)$, thus, in the water solution of a mixture of melamine and citric acid the proton of one dissociated carboxyl group is accepted by ring nitrogen atom with lone-pair of electron of melamine ring with the formation of melaminium cation.

The aromatic six-membered ring of singly protonated melaminium moiety in the crystal is planar, but shows a noticeable distortion from the ideal hexagonal form. The protonation of melamine ring at the nitrogen atom is evidenced by the increasing in the ring angle at the protonated N-ring atom (C–N1–C, 118.77(8)°) in relation to the non-protonated melamine ring (116.0°) [15]. The internal C–N1–C angle at the protonated nitrogen atom is significantly larger than the other two C–N–C angles and the internal N–C–N angle containing only non-protonated N atoms is significantly greater than the other two N–C–N angles containing both protonated and non-protonated nitrogen atoms. This is a result of the steric effect of a lone-pair of electrons, predicted by the valence-shell electron pair repulsion model (VSEPR) [31,32]. The *ab-initio* gas-phase geometry calculated for the isolated melaminium cation shows similar correlation between the C–N–C and N–C–N angles within the ring (see Table 3). Thus,

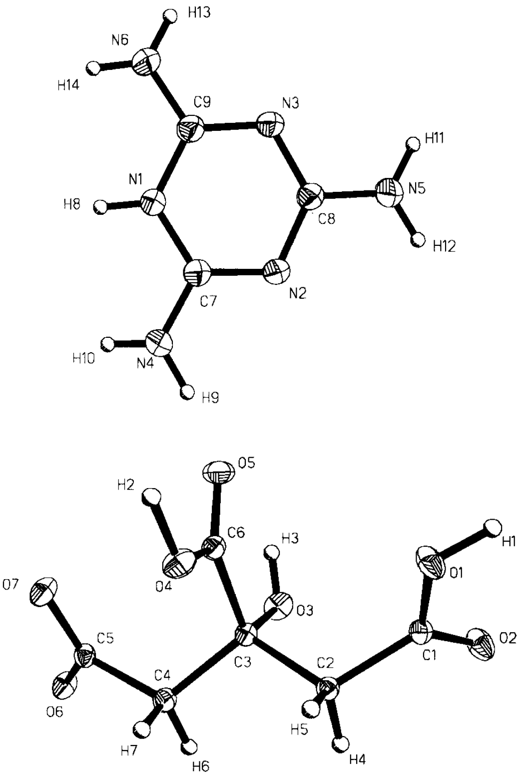


**Figure 1.** View of the melaminium(+) and dihydrogencitrate(–) ions with the labelling scheme. Thermal ellipsoids are shown at a probability level of 50%. H atoms are shown as spheres with arbitrary radii.

the ring distortion results mainly from the steric effect of the lone-pair of electrons on the ring N atoms and, to a lesser degree, from the hydrogen-bonding system, intermolecular interactions and crystal packing.

**Table 2.** Final atomic coordinates and equivalent isotropic displacement parameter for melaminium dihydrogencitrate, $U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i a_j \mathbf{a}_i\mathbf{a}_j$ (Å$^2$).

| Atom | x | y | z | $U_{\mathrm{eq}}$ |
|---|---|---|---|---|
| O1 | 1.18736(15) | 0.21042(4) | 0.52738(7) | 0.0351(2) |
| O2 | 0.97498(16) | 0.13605(4) | 0.41279(7) | 0.0374(2) |
| O3 | 0.56865(13) | 0.24719(4) | 0.37792(8) | 0.0324(2) |
| O4 | 1.04960(13) | 0.35980(4) | 0.46961(7) | 0.0315(2) |
| O5 | 0.74645(15) | 0.32150(4) | 0.55889(7) | 0.0354(2) |
| O6 | 0.29862(13) | 0.38078(4) | 0.19233(7) | 0.0326(2) |
| O7 | 0.54826(14) | 0.41811(4) | 0.35289(7) | 0.0350(2) |
| C1 | 1.04646(16) | 0.19093(4) | 0.42767(8) | 0.0225(2) |
| C2 | 0.98026(17) | 0.24206(4) | 0.33367(8) | 0.0213(2) |

Table 2 (continuation)

| | | | | |
|---|---|---|---|---|
| C3 | 0.77027(16) | 0.28576(4) | 0.36015(8) | 0.0205(2) |
| C4 | 0.69148(18) | 0.32952(5) | 0.25081(8) | 0.0257(2) |
| C5 | 0.49858(17) | 0.37954(4) | 0.26785(8) | 0.0243(2) |
| C6 | 0.85422(17) | 0.32478(4) | 0.47396(8) | 0.0237(2) |
| N1 | –0.00863(15) | 0.51552(4) | 0.77182(7) | 0.0253(2) |
| C7 | 0.19431(18) | 0.50813(4) | 0.85879(8) | 0.0243(2) |
| N2 | 0.36648(15) | 0.46493(4) | 0.84976(7) | 0.0255(2) |
| C8 | 0.32986(17) | 0.42881(4) | 0.74986(8) | 0.0237(2) |
| N3 | 0.13795(15) | 0.43513(4) | 0.65801(7) | 0.0262(2) |
| C9 | –0.02996(18) | 0.47914(4) | 0.67085(8) | 0.0241(2) |
| N4 | 0.21580(19) | 0.54599(5) | 0.95289(8) | 0.0354(2) |
| N5 | 0.49407(19) | 0.38401(5) | 0.73920(9) | 0.0368(2) |
| N6 | –0.22260(17) | 0.48919(5) | 0.58628(8) | 0.0320(2) |
| H1 | 1.222(3) | 0.1776(8) | 0.581(2) | 0.063(5) |
| H2 | 1.090(3) | 0.3845(9) | 0.543(2) | 0.072(5) |
| H3 | 0.544(3) | 0.2551(8) | 0.448(2) | 0.054(5) |
| H4 | 0.922(2) | 0.2195(6) | 0.256(2) | 0.032(3) |
| H5 | 1.128(2) | 0.2663(6) | 0.329(2) | 0.032(3) |
| H6 | 0.626(2) | 0.3020(6) | 0.180(2) | 0.037(3) |
| H7 | 0.843(3) | 0.3528(7) | 0.243(2) | 0.048(4) |
| H8 | –0.114(3) | 0.5474(8) | 0.782(2) | 0.053(4) |
| H9 | 0.350(3) | 0.5421(7) | 1.015(2) | 0.049(4) |
| H10 | 0.098(3) | 0.5731(7) | 0.963(2) | 0.047(4) |
| H11 | 0.481(3) | 0.3626(7) | 0.670(2) | 0.047(4) |
| H12 | 0.623(3) | 0.3771(7) | 0.799(2) | 0.042(4) |
| H13 | –0.244(3) | 0.4642(7) | 0.526(2) | 0.041(4) |
| H14 | –0.332(3) | 0.5189(7) | 0.599(2) | 0.048(4) |

**Table 3.** Comparison of the X-ray and gas-phase geometry of melaminium dihydrogencitrate.

***Melaminium cation***

| Bond lengths [Å] and angles [deg] | X-ray | HF/6-31G(d,p) |
|---|---|---|
| N1–C7 | 1.3658(13) | 1.367 |
| N1–C9 | 1.3570(12) | 1.367 |
| N2–C7 | 1.3281(12) | 1.308 |
| N2–C8 | 1.3418(12) | 1.341 |
| N3–C8 | 1.3555(12) | 1.341 |
| N3–C9 | 1.3318(12) | 1.308 |
| N4–C7 | 1.3122(13) | 1.323 |
| N5–C8 | 1.3232(13) | 1.315 |

Table 3 (continuation)

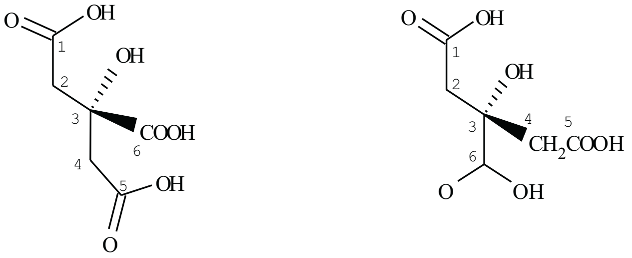
| | | |
|---|---|---|
| N6–C9 | 1.3183(13) | 1.323 |
| C7–N1–C9 | 118.77(8) | 118.7 |
| C7–N2–C8 | 116.08(8) | 116.6 |
| C8–N3–C9 | 116.91(8) | 116.7 |
| N1–C7–N2 | 122.18(8) | 121.6 |
| N2–C8–N3 | 124.89(9) | 125.5 |
| N3–C9–N1 | 121.07(9) | 121.3 |
| ***Dihydrogencitrate anion*** | | |
| O1–H1 | 0.918(18) | 0.967 |
| O1–C1 | 1.3172(12) | 1.334 |
| O2–C1 | 1.2137(12) | 1.203 |
| C1–C2 | 1.5043(13) | 1.507 |
| C2–C3 | 1.5460(12) | 1.543 |
| C3–C4 | 1.5362(13) | 1.545 |
| C3–C6 | 1.5234(12) | 1.537 |
| C4–C5 | 1.5283(13) | 1.548 |
| O3–C3 | 1.4175(11) | 1.392 |
| O3–H3 | 0.840(17) | 0.987 |
| O4–C6 | 1.3126(12) | 1.341 |
| O4–H2 | 0.966(19) | 0.967 |
| O5–C6 | 1.2148(12) | 1.195 |
| O6–C5 | 1.2743(12) | 1.225 |
| O7–C5 | 1.2461(12) | 1.237 |
| O1–C1–O2 | 122.68(8) | 121.8 |
| O4–C5–O5 | 125.47(9) | 122.2 |
| O6–C5–O7 | 123.50(9) | 127.2 |
| O1–C1–C2 | 114.77(8) | 112.9 |
| O2–C1–C2 | 122.55(9) | 125.7 |
| C1–C2–C3 | 112.43(8) | 114.3 |
| C2–C3–C4 | 108.29(7) | 109.4 |
| C2–C3–C6 | 110.39(7) | 110.4 |
| C2–C2–O3 | 109.15(7) | 107.1 |
| C3–O3–H3 | 106.2(11) | 105.1 |
| C3–C6–O5 | 121.01(9) | 126.3 |
| C3–C6–O4 | 113.51(8) | 112.5 |
| C3–C4–C5 | 114.35(8) | 115.0 |
| C4–C5–O6 | 118.28(8) | 115.6 |
| C4–C5–O7 | 118.18(8) | 115.3 |
| C4–C3–C6 | 111.21(8) | 109.1 |
| C6–C3–O3 | 108.48(8) | 109.5 |
| C1–O1–H1 | 111.0(11) | 108.4 |

Table 3 (continuation)

| ***Torsion angles [deg]*** | | |
|---|---|---|
| H1–O1–C1–O2 | –179.7(12) | 7.4 |
| O1–C1–C2–C3 | –79.4(1) | 59.6 |
| O2–C1–C2–C3 | 100.4(1) | –123.4 |
| C1–C2–C3–C4 | 170.5(1) | –172.1 |
| C2–C3–C4–C5 | –175.2(2) | –171.9 |
| C3–C4–C5–O6 | –123.8(1) | –153.8 |
| C3–C4–C5–O7 | 58.2(1) | 28.2 |
| O3–C3–C6–O5 | –2.6(1) | 6.6 |
| O3–C3–C6–O4 | 176.5(1) | –174.5 |
| C2–C3–C6–O5 | –122.1(1) | 124.4 |
| C2–C3–C6–O4 | 57.0(1) | –56.6 |
| C2–C3–O3–H3 | 120.0(11) | 162.1 |
| C4–C3–C6–O4 | –63.3(1) | 63.3 |
| C4–C3–C6–O5 | 117.6(1) | –115.5 |
| C4–C3–O3–H3 | –121.7(12) | 42.4 |
| C1–C2–C3–C6 | 66.2(1) | –69.5 |
| C1–C2–C3–O3 | –52.9(1) | 49.6 |

The anhydric citric acid [33,34] and monohydrate [35,36], as well as several salts [37] have been studied by X-ray technique. The citric acid has four ionisable groups, three carboxyl groups with $pK_1 = 3.13$, $pK_2 = 4.76$, $pK_3 = 6.40$, and one hydroxyl group with a $pK_4$ greater than 11 [38]. In the solid state it was found that the central carboxyl group ($\alpha$ to a hydroxyl group) is ionized first, than the two terminal carboxyl groups, and finally the hydroxyl group [38]. This is in contrast to the present crystal of melaminium dihydrogencitrate, in which one of the terminal carboxyl group of citric acid is ionized (Figure 1b) as clearly evidence the carbon-oxygen distances (see Table 3). Among the structures determined on single crystals [36], there are two conformations of citrates (see Scheme 2). The backbone of citrate carbon chain from C1 to C5 may be fully extended, *i.e.* both torsion angles C1–C2–C3–C4 and C2–C3–C4–C5 are near 180° in almost planar zigzag chain (conformation I) or one of the carbon atoms (C1 or C5) may be swung, yielding the conformation II (one of the torsion angles of C1–C2–C3–C4 and C2–C3–C4–C is near ±60°). In the crystal of melaminium dihydrogencitrate, studied here, the dihydrogencitrate(–) anion adopts the conformation I, both torsion angles (C1–C2–C3–C4 and C2–C3–C4–C5) are near 180° (see Table 3). The C3–C6 and C4–C5 bonds are typically longer than the value of 1.511 Å normally found for a $C(sp^3)–C(sp^2)$ bond [39], and they are longer than C1–C2 bond (1.504(1) Å). This lengthening of a carbon-carbon bond is reminiscent of the *polymethine state*, described in details for the $sp^2$ carbon atoms in [40]. *Ab-initio* calculation shows that the gas-phase conformation of dihydrogencitrate(–) anion is very similar to that found in the crystal. Both torsion angles describe the conformation of the carbon chain, *i.e.* C1–C2–C3–C4 and C2–C3–C4–C5 are near ±180° (–172.1 and –171.9°, respectively). As show the theoretical molecular orbital calculations, the conformation I of dihydrogencitrate(–) ion is more stable than conformation II. Modelling calculation of the conformation II of dihydrogencitrate(–) anion (the C1–C2–C3–C4 torsion angle was fixed at 60°) shows, that this conformation is less stable (~8.5 kcal/mol in relation to the conformation I). The orientation of the terminal ionized carboxyl group (COO$^-$) in relation to the carbon chain describing by the torsion angle of O6–C5–C4–C3 is similar in X-ray and in gas-phase molecule, while the non-ionized carboxyl group (COOH) is oppositely rotated in the X-ray geometry in relation to the *ab-initio* gas-phase. The rotation of the terminal non-ionized carboxyl group COOH, described by the torsion angle of O1–C1–C2–C3, is equal to –79.4(1)° in the crystal and +59.6° in the gas-phase. Thus, the terminal COO$^-$ and COOH groups are not coplanar with the carbon chain (Table 3). The central carboxyl group is almost coplanar with the hydroxyl group in both X-ray experimental and *ab-initio* calculated geometry, due to the intramolecular H3$\cdots$O5 interaction that stabilize this planar conformation.

Scheme 2

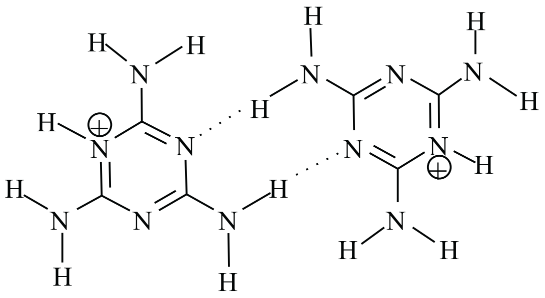


(I) (II)

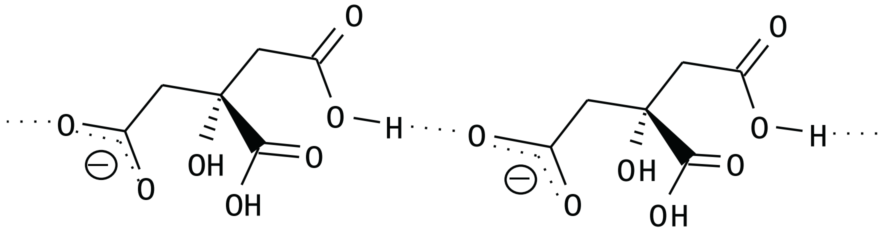
The schematic representation of the seven types of hydrogen-bonded motifs I–VII, observed in the crystal of melaminium dihydrogencitrate, is shown in Scheme 3. In the crystal all hydrogen atoms of the singly protonated melaminium cation are involved in the hydrogen bonds, and the two non-protonated N-ring atoms with the lone-pair of electrons take place in the hydrogen bonds as acceptor H, thus, the melaminium(+) moiety is involved into nine hydrogen bonds. In contrast to the all known structures of singly protonated melaminium salts [17,18,20–23,26], in which the melaminium(+) moieties form one dimensional hydrogen bonded linear chains, as schematically illustrated in the Scheme 1(b), in this crystal the melaminium moiety interacts with neighbouring in a near linear fashion through a pair of N–H$\cdots$N hydrogen bonds (see Table 4) to form a planar dimeric structure (motif I).

The dihydrogencitrate(–) anions are linked through of O–H$\cdots$O hydrogen bonds (motif II) to form a zigzag infinite chain (see Figure 2). The dihydrogencitrate(–) anions linked each to other in head-to-tail fashion into chains that are interconnected *via* the hydrogen bonds of hydroxyl groups (motif III) into two-dimensional network, which is parallel to the *ac* plane (see Figure 3). In the crystal the centro-symmetrically

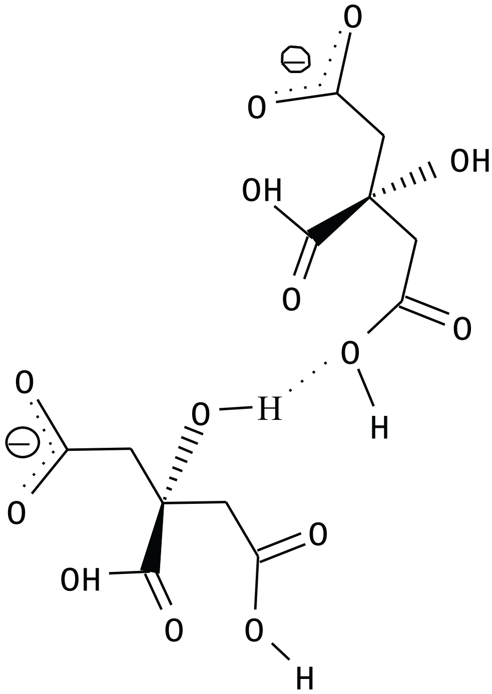
Scheme 3



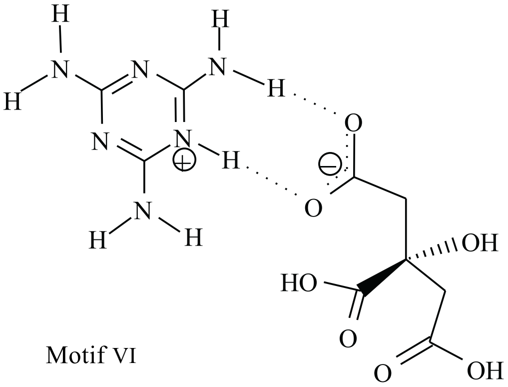
Motif I



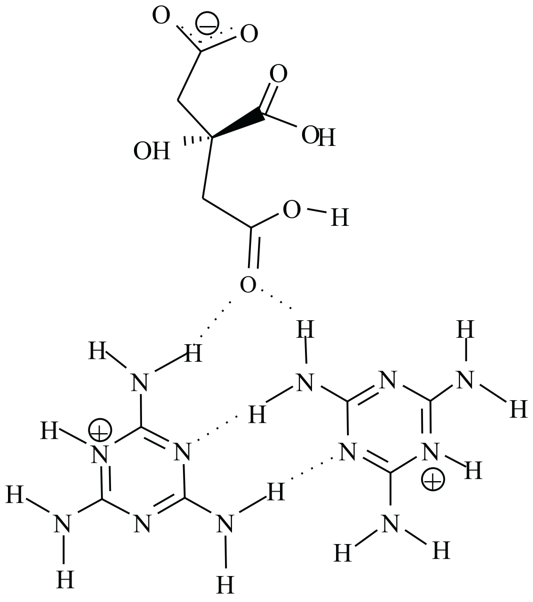
Motif II



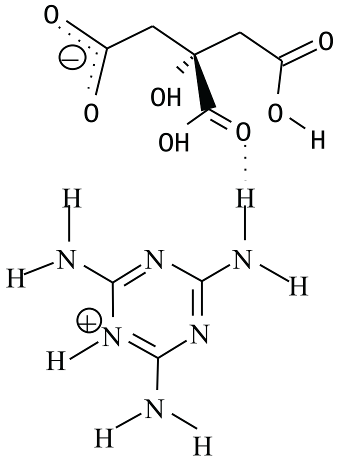
Motif III



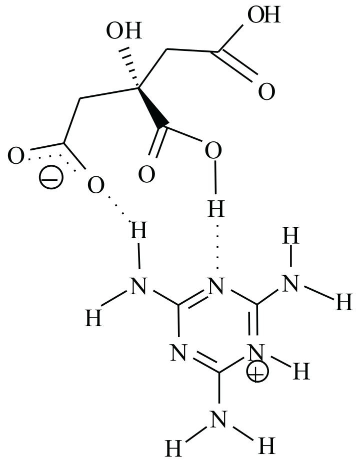
Motif VI



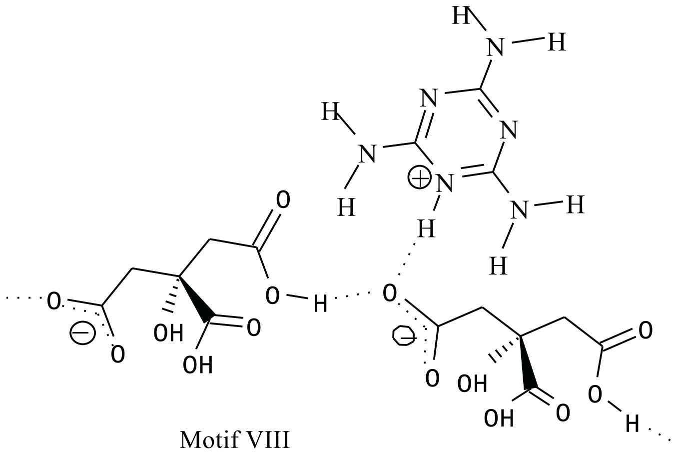
Motif V



Motif VI



Motif VII



Motif VIII

paired dimers of melaminium moieties through two almost linear N–H···N hydrogen bonds interact *via* more bent N–H···O (motif IV–VII) and N···H–O (motif VIII) hydrogen bonds with the dihydrogencitrate(–) ions to form hydrogen bonded three dimensional network (see Figure 4a), and one of the corrugated sheets that is parallel to the (102) plane is illustrated in Figure 4b. The oxygen atom (O2) of non-dissociated terminal carboxyl group (COOH) is involved in bifurcated hydrogen bond (motif V) with two hydrogen atoms of dimeric structure of melaminium(+) cations. In a similar bifurcated hydrogen bond involves the oxygen atom (O6) of ionized terminal carboxyl group of dihydrogencitrate(–), however, it is acceptor of two hydrogen atoms, one with the hydrogen of carboxyl group of neighbouring dihydrogencitrate(–) ion and the other with the hydrogen of the protonated N-ring atom (motif VIII). The geometric parameters of the hydrogen bonds are collected in Table 4.

**Table 4.** Hydrogen bonding geometry (Å,°).

| *D–H···A* | *D–H* | *H···A* | *D···A* | <(*D–H···A*) |
|---|---|---|---|---|
| O1–H1···O6$^{i}$ | 0.91(2) | 1.75(2) | 2.659(2) | 175(2) |
| O4–H2···N3$^{ii}$ | 0.97(2) | 1.66(2) | 2.621(2) | 172(2) |
| O3–H3···O5 | 0.84(2) | 2.06(2) | 2.617(2) | 123(2) |
| O3–H3···O1$^{iii}$ | 0.84(2) | 2.49(2) | 3.018(2) | 122(2) |
| N1–H8···O6$^{iv}$ | 0.91(2) | 1.85(2) | 2.765(2) | 173(2) |
| N4–H9···N2$^{v}$ | 0.93(2) | 2.00(2) | 2.927(2) | 179(2) |
| N4–H10···O2$^{vi}$ | 0.88(2) | 2.02(2) | 2.738(2) | 138(2) |
| N5–H11···O5 | 0.90(2) | 2.25(2) | 2.962(2) | 136(2) |
| N5–H12···O2$^{vii}$ | 0.91(2) | 2.16(2) | 3.047(2) | 168(2) |
| N6–H13···O7$^{iii}$ | 0.85(2) | 2.30(2) | 3.096(2) | 156(2) |
| N6–H14···O7$^{iv}$ | 0.90(2) | 1.92(2) | 2.808(2) | 173(2) |

Symmetry code: (*i*) 1 + x, 1/2 – y, 1/2 + z; (*ii*) 1 + x, y, z; (*iii*) x – 1, y, z; (*iv*) –x, 1 – y, 1 – z; (*v*) 1 – x, 1 – y, 2 – z; (*vi*) 1 – x, 1/2 + y, 1½ – z; (*vii*) x, 1/2 – y, 1/2 + z.

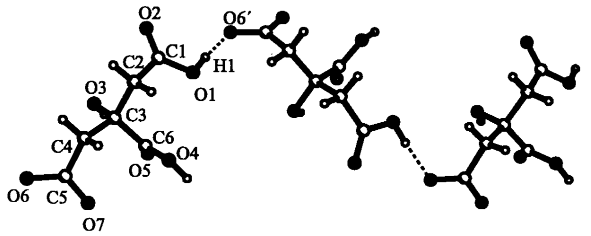


**Figure 2.** View of the infinite zigzag chain of the head-to-tail interacted dihydrogencitrate(–) anions (carboxyl-carboxylate interaction).

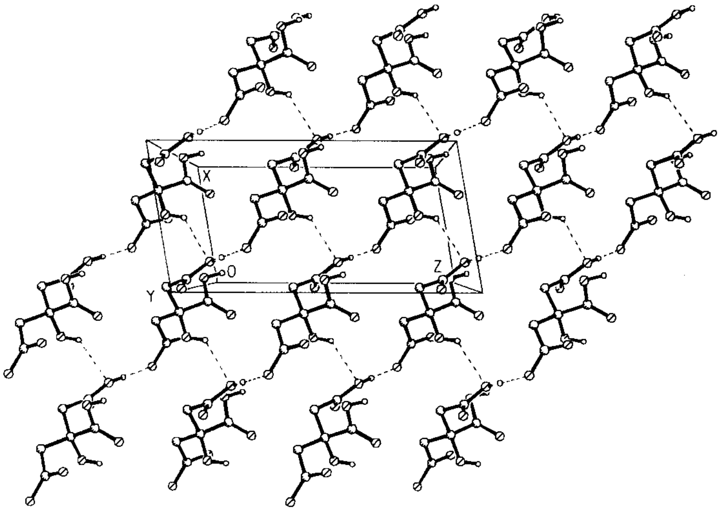
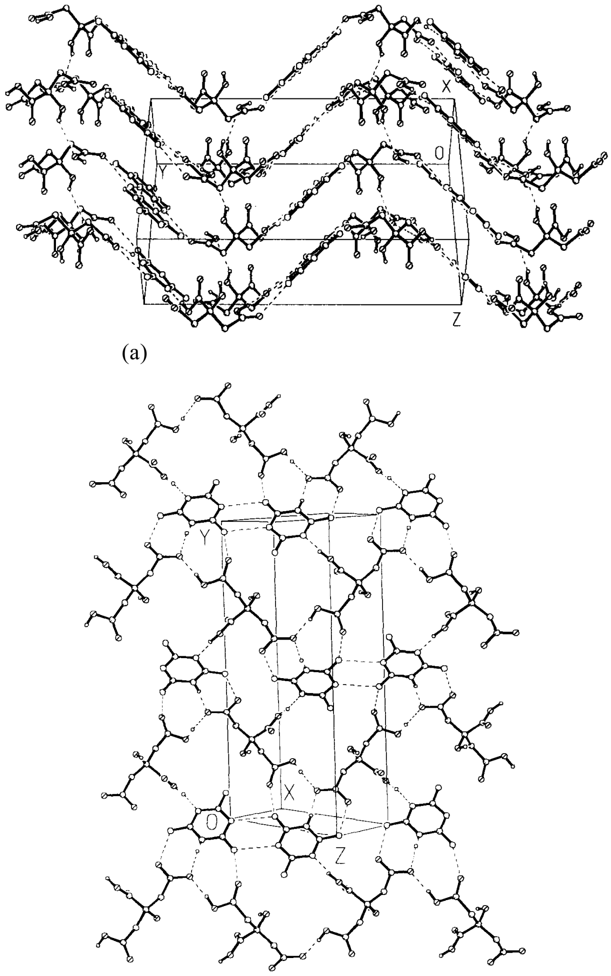


**Figure 3.** Two-dimensional sheet of dihydrogencitrate(–) chains interconnected *via* hydrogen bond of the hydroxyl groups (*ac*-plane).



(a)

(b)

**Figure 4.** Packing diagram of hydrogen bonded three-dimensional network (a) and one of the corrugated layer of hydrogen bonded melaminium(+) and dihydrogencitrate(–) ions (b). H atoms of methylene ($CH_2$) and amine ($NH_2$) groups are omitted for clarity.

***Supplementary material.*** Additional material comprising full details of the X-ray data collection and final refinement parameters, including anisotropic thermal parameters and a full list of the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Center in the CIF format as supplementary publications no. CCDC 204596. Copies of the data can be obtained free of charge on the application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK, (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

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