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Crystal structures of dihydroxyacetone and its derivatives

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Abstract—The crystal and molecular structures of three crystalline forms of the dihydroxyacetone dimer, $C_6H_{12}O_6$, DHA-dimer: α (**1a**), β (**1b**), and γ (**1c**), the hydrated calcium chloride complex of dihydroxyacetone monomer, $CaCl_2(C_3H_6O_3)_2{\cdot}H_2O$, $CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**), the tetrahydrated calcium chloride complex of dihydroxyacetone monomer, $CaCl_2(C_3H_6O_3){\cdot}4H_2O$, $CaCl_2(DHA){\cdot}4H_2O$ (**2b**), the dihydroxyacetone monomer, $C_3H_6O_3$, DHA (**2c**), and dihydroxyacetone dimethyl acetal, $C_5H_{12}O_4$, $(MeO)_2$DHA (**3**) are described. Compounds **1a** and **2b** crystallize in the triclinic system, and **1b**,**c**, **2a**,**c**, and **3** are monoclinic. Molecules of all forms of dihydroxyacetone dimer **1a**,**b**, and **1c** are the *trans* isomers, with the 1,4-dioxane ring in the chair conformation and the hydroxyl and hydroxymethyl groups in axial and equatorial dispositions, respectively. The Ca^{2+} ions in **2a** and **2b** are bridged by the carbonyl O atoms from two symmetry-related DHA molecules to form centrosymmetric dimers with Ca···Ca distance of 4.307(2) Å in **2a** and 4.330(2) and 4.305(2) Å in two crystallographically independent dimers in **2b**. DHA molecules coordinate to the Ca^{2+} ions by hydroxyl and carbonyl oxygen atoms. The eight-coordinate polyhedra of Ca^{2+} are completed by water molecule and Cl^- ion in **2a** and by four water molecules in **2b**. The dihydroxyacetone molecules in **2a**,**b**, and **2c** are in an extended conformation, with both hydroxyl groups being *synperiplanar* (*sp*) to the carbonyl O atom. All hydroxyl groups in **2c** (along with water molecules in **2a** and **2b**) are involved as donors in medium strong and weak intermolecular O–H···O hydrogen bonding. Some of them, as well as carbonyl O atoms or Cl^- ions in **2a** and **2b**, act as acceptors in C–H···O (and C–H···Cl) hydrogen interactions.

Keywords: Sugars; Ketotriose; Dihydroxyacetone; DHA; Dihydroxyacetone dimer; Ca coordination; O–H···O hydrogen bonds; O–H···Cl hydrogen bonds; C–H···O, C–H···Cl interactions

1. Introduction

1,3-Dihydroxy-2-propanone (commonly called dihydroxyacetone, DHA) is the simplest ketose, a ketotriose. No crystal structures of the aldo- and keto-trioses and tetroses are yet known. A notable exception is the aldotriose, D-glyceraldehyde, the dimeric crystal structure of which has been described in 1973 by Senma et al.[1] We hope that crystal and molecular structure of dihydroxyacetone, the ketotriose described here in dimeric as well as in monomeric form, along with some its derivatives, may enrich the literature of carbohydrate chemistry. Some aspects of DHA have been long known; the investigation of dihydroxyacetone structure in solution made by Davis in 1973 established that commercial, solid dihydroxyacetone, which is 100% in the dimeric form, dissociates in water solution into a mixture of two monomeric forms: the free carbonyl and the hydrate (*gem*-diol) in a ratio 4:1.[2] Nevertheless the crystal structure of DHA has not yet been described in the literature. We undertook the solid-state investigation to complete our research into dihydroxyacetone phosphate (DHAP) and its derivatives. DHAP is an important biochemical intermediate that acts in the main metabolic pathways, such as gluconeogenesis, fructose metabolism, synthesis of triacylglycerols, and phospholipids, the glycerophosphate shuttle, and in glycolysis. Dihydroxyacetone phosphate is a substrate for many enzymes, including triosephosphate isomerase, glycerol-3-phosphate dehydrogenase, and several aldolases.

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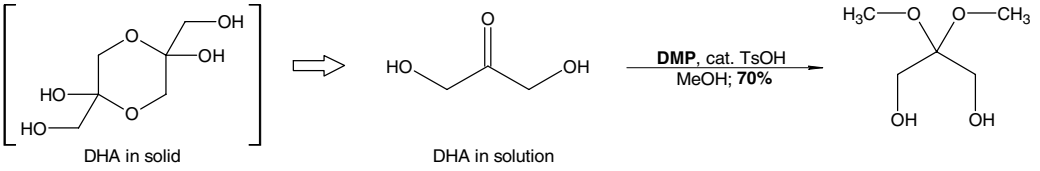
Some of the known aldolases (which have been commonly used for the synthesis of synthetic sugars and related chiral compounds) accept a broad spectrum of aldehydes, but all of them are very specific to DHAP.[3–9]

As it is known that dihydroxyacetone exists as a dimer in solid state, we tried to obtain X-ray quality crystals by recrystallizing the commercially available compound from several solvents. This gave us two different crystalline forms (polymorphs) of dihydroxyacetone dimer: form α (**1a**) and β (**1b**). Then, encouraged by the suggestion of Yuasa et al.[10] that addition of calcium ions to the solution of DHA stabilizes the *cis*-dimer form, we tried to obtain this complex in the solid state. We obtained crystals of two different hydrated calcium chloride complexes of dihydroxyacetone monomer, namely, **2a** and **2b**. With this encouraging result in hand and following the Davis report,[2] we obtained crystals of dihydroxyacetone monomer (**2c**) by lyophilization of the frozen aqueous solution of commercial DHA. It turned out later, that quite good quality crystals of **2c** (and sometimes also of **1a**) could be obtained by decreasing the rate of the lyophilization process. At the same time another type of crystals is formed, very thin tear-shape plates of the next polymorph of (DHA-dimer)—γ form (**1c**).

Since DHAP itself is unstable and expensive, improvement of the chemical syntheses of its stable precursors, that may be stored indefinitely, has been an objective. The best of these is the dimethyl acetal of dihydroxyacetone phosphate, which we have obtained using a slightly modified method described earlier by Ferroni et al.[11] The modification concerns mainly the first step of this method: synthesis of dihydroxyacetone dimethyl acetal (**3**), whose structure we also



Scheme 1. Synthesis scheme for compound **3**. DMP = 2,2-dimethoxypropane.

Table 1. Principal interatomic distances (Å), and torsion angles (°) in **1a**,**b**, and **1c** (standard deviations in parentheses)

α-(DHA-dimer) (**1a**)		β-(DHA-dimer) (**1b**)		γ-(DHA-dimer) (**1c**)	
Selected bond lengths					
C-1–O-1	1.421(2)	C-1–O-1; C-11–O-11	1.420(2); 1.413(2)	C-1–O-1	1.434(2)
C-2–O-2	1.412(2)	C-2–O-2; C-21–O-21	1.405(2); 1.406(2)	C-2–O-2	1.420(2)
C-2–O-3^i	1.419(2)	C-2–O-31; C-21–O-3	1.427(2); 1.428(2)	C-2–O-3^i	1.421(2)
C-3–O-3	1.428(2)	C-3–O-3; C-31–O-31	1.435(2); 1.428(2)	C-3–O-3	1.431(2)
Endocyclic torsion angles					
C-2–C-3–O-3–C-2^i	−56.2(2)	C-2–C-3–O-3–C-21	−55.3(2)	C-2–C-3–O-3–C-2^i	−54.1(2)
O-3–C-3–C-2–O-3^i	54.5(2)	O-3–C-3–C-2–O-31	55.0(2)	O-3–C-3–C-2–O-3^i	52.1(2)
C-3–O-3–C-2^i–C-3^i	55.3(2)	C-3–O-3–C-21–C-31	53.6(2)	C-3–O-3–C-2^i–C-3^i	53.5(2)
		C-2–O-31–C-31–C-21	57.8(2)		
		O-3–C-21–C-31–O-31	−54.2(2)		
		C-3–C-2–O-31–C-31	−57.0(2)		
Orientation of the hydroxyl and hydroxymethyl substituents					
O-1–C-1–C-2–O-3^i	−65.6(2)	O-1–C-1–C-2–O-31	−69.6(2)	O-1–C-1–C-2–O-3^i	168.0(2)
O-1–C-1–C-2–C-3	175.2(2)	O-1–C-1–C-2–C-3	172.3(2)	O-1–C-1–C-2–C-3	48.6(2)
O-1–C-1–C-2–O-2	55.2(2)	O-1–C-1–C-2–O-2	51.5(2)	O-1–C-1–C-2–O-2	−72.4(2)
O-2–C-2–O-3^i–C-3^i	63.2(2)	O-2–C-2–O-31–C-31	62.2(2)	O-2–C-2–O-3^i–C-3^i	65.0(2)
O-2–C-2–C-3–O-3	−65.6(2)	O-2–C-2–C-3–O-3	−65.8(2)	O-2–C-2–C-3–O-3	−68.5(2)
C-1–C-2–O-3^i–C-3^i	−175.0(1)	C-1–C-2–O-31–C-31	−176.2(2)	C-1–C-2–O-3^i–C-3^i	−174.3(2)
C-1–C-2–C-3–O-3	172.0(2)	C-1–C-2–C-3–O-3	171.3(2)	C-1–C-2–C-3–O-3	167.7(2)
		O-11–C-11–C-21–O-3	−56.2(2)		
		O-11–C-11–C-21–C-31	63.6(2)		
		O-11–C-11–C-21–O-21	−173.5(2)		
		O-21–C-21–O-3–C-3	−70.1(2)		
		O-21–C-21–C-31–O-31	68.4(2)		
		C-11–C-21–O-3–C-3	175.3(2)		
		C-11–C-21–C-31–O-31	−172.2(2)		

Symmetry codes: (*i*) $-x+1, -y+1, -z+1$.

describe here. Replacing the trimethyl orthoformate, $HC(OMe)_3$ (from the original method) with 2,2-dimethoxypropane (DMP) allowed us to increase the yield of the reaction from 41% to 70% (Scheme 1). Other reaction conditions (time, temperature) were kept as in the original paper.[11]

2. Results and discussion

2.1. Dihydroxyacetone dimer, α (1a), β (1b), and γ (1c)

Commercial dihydroxyacetone (Aldrich) crystallizes, as a dimer, from both water and 2-propanol, as well as during the lyophilization process, with a 1,4-dioxane ring in the chair conformation (Table 1). The (DHA-dimer) molecules in **1a** and **1c** crystals lie on an inversion center, while those in **1b** are not centrosymmetric. All molecules are the *trans* isomers with the more electronegative hydroxyl groups in axial positions and hydroxymethyl groups equatorial because of the anomeric effect (Fig. 1). This observation is consistent with the investigation of the DHA structure in solution.[2] The exocyclic, anomeric C-2–O-2 (along with C-21–O-21 in **1b**) distances are shortened much more significantly in **1b** than in **1a** and **1c** (Table 1). In **1a** and **1c** the anomeric shortening is accompanied by the similar shortening of the adjacent, ring C-2–O-3^i bonds with the other endocyclic C-3–O-3 distance being slightly longer, whereas in **1b** the differences between both anomeric and four ring C–O bonds are much more noticeable.

The orientation of the hydroxymethyl groups relative to the dioxane ring is different in the three presented forms of (DHA-dimer) (Fig. 2, Table 1). We find these groups in a *gauche-trans* (*gt*) orientation in **1a**, whereas in **1c** they are in a *trans-gauche* (*tg*) conformation. In the molecule of **1b**, which does not lie on the inversion center, two of the hydroxymethyl groups are in a different arrangement; one in the *gauche–trans* (*gt*) as in **1a**, and another one in a *gauche–gauche* (*gg*) arrangement. The respective conformations are characterized by the pairs of torsion angles O-1–C-1–C-2–O-3^i, O-1–C-1–C-2–C-3 for **1a** and **1c** and O-1–C-1–C-2–O-31, O-1–C-1–C-2–C-3, and O-11–C-11–C-21–O-3, O-11–C-11–C-21–C-31 for **1b**. A result of this conformation is the different orientation of hydroxyl and hydroxymethyl groups in relation to each other in the molecules

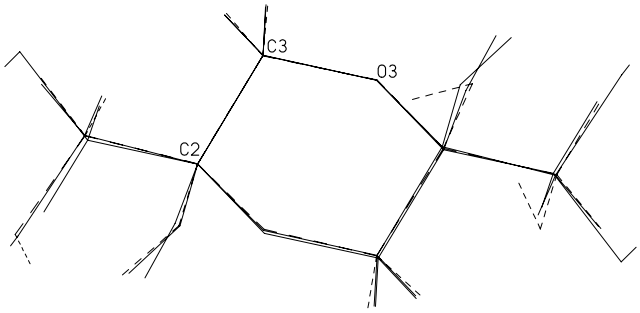


Figure 2. Comparison of the (DHA-dimer) molecular structures in **1a**–**c** showing different orientation of the hydroxymethyl groups in relation to the 1,4-dioxane ring: (*gt*) in **1a**, (*gt*), (*gg*) in **1b** (dashed line) and (*tg*) in **1c**. The common reference points are O-3, C-2, and C-3.

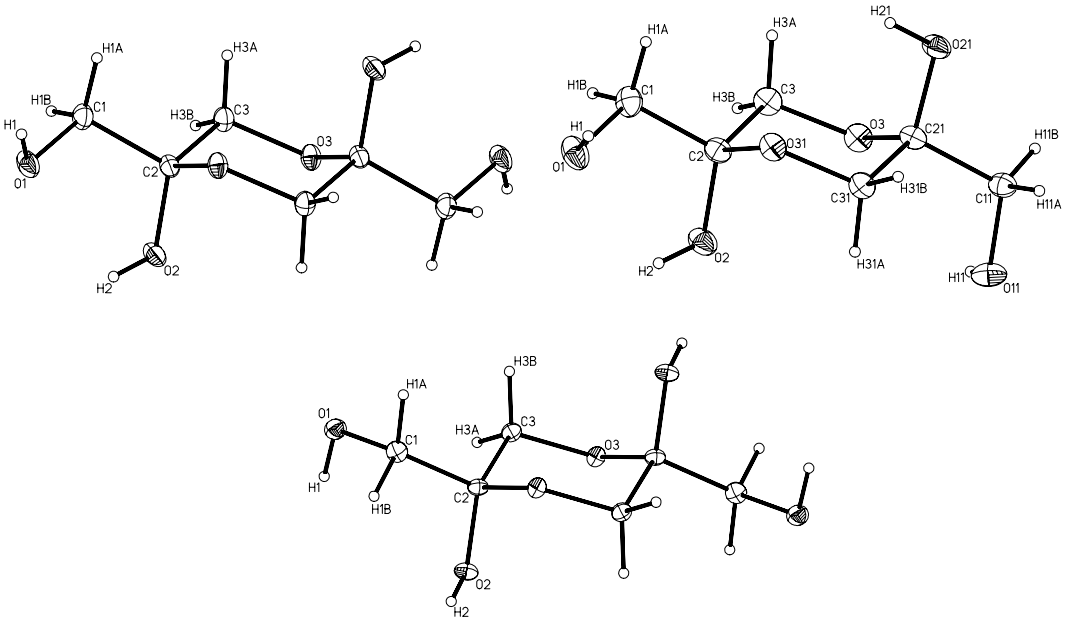


Figure 1. The molecular structure and the atom-numbering scheme for DHA-dimer molecules in **1a** (top, left), **1b** (top, right), and **1c** (bottom). Displacement ellipsoids are shown at 20% probability level. The H atoms are drawn as small circles of arbitrary radii.

described. Both ring-bonded, axially oriented hydroxyls in **1a** and **1c** and one of them in **1b**, are almost *gauche* to the hydroxymethyl groups whereas the (*gg*) conformation around C-11–C-21 in **1b** implies nearly *antiperiplanar* (*ap*) (*trans*) orientation of O-11 relative to O-21.

The same chair conformation of the 1,4-dioxane ring was also found in the dimeric form of dihydroxyacetone diethyl acetal, *trans*-2,5-diethoxy-2,5-bis(hydroxymethyl)-1,4-dioxane,[12] where both DHA hydroxyl groups have been replaced by ethoxyl. In this dimeric acetal molecule, two bulky $-OCH_2CH_3$ groups are in the more-crowded axial positions and the C–O bond lengths distribution is similar to that found in **1a** and **1b**. The orientation of the hydroxymethyl substituents in relation to the dioxane ring is similar to that observed in **1c**, namely *trans-gauche*.

The crystal structures of **1a**,**b**, and **1c** are stabilized by, medium strong, and weak, intermolecular O–H···O hydrogen bonds and C–H···O contacts (Table 2). A typical motif in all three crystals is mutual linking of hydroxyl and hydroxymethyl groups from symmetry-related molecules [simultaneous existence of $-CH_2-O-H\cdots O(H)$ and $O-H\cdots O(H)-CH_2-$ interactions]. In **1a** and **1b** additional intramolecular O-2–H-2···O-1 contacts occur so that the three-center hydrogen bonds are formed. Packing diagrams for β- and γ-(DHA-dimer) **1b** and **1c**, in which only the O–H···O bonds are marked, are shown in Fig. 3. The three-dimensional O–H···O hydrogen-bond network is the characteristic of **1b** and **1c**, whereas adjacent DHA molecules in **1a** are linked by O–H···O and C–H···O hydrogen bonds to form a two-dimensional network with well defined layers parallel to $(1\,0\,\bar{1})$ plane (Fig. 4).

Table 2. Geometry of proposed hydrogen bonds and close C–H···O contacts for **1a**,**b**, and **1c**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
α-*(DHA)*$_2$ (**1a**)				
O-1–H-1···O-2^{i}	0.81(2)	2.04(2)	2.826(2)	163(2)
O-2–H-2···O-1	0.82(2)	2.42(2)	2.827(2)	112(2)
O-2–H-2···O-1^{ii}	0.82(2)	2.02(2)	2.754(2)	150(2)
C-1–H-1A···O-3^{i}	0.96(2)	2.50(2)	3.308(3)	142(2)
β-*(DHA)*$_2$ (**1b**)				
O-1–H-1···O-21^{iii}	0.87(3)	1.93(3)	2.798(2)	174(2)
O-2–H-2···O-1	0.91(3)	2.34(3)	2.799(2)	111(2)
O-2–H-2···O-1^{iv}	0.91(3)	2.12(3)	2.894(2)	144(2)
O-11–H-11···O-3^{v}	0.80(2)	2.06(2)	2.756(3)	145(2)
O-21–H-21···O-11^{vi}	0.87(3)	1.78(3)	2.627(2)	166(2)
C-1–H-1B···O-21^{vii}	1.02(2)	2.53(2)	3.546(3)	174(2)
C-11–H-11A···O-2^{viii}	0.97(2)	2.61(2)	3.579(3)	176(2)
γ-*(DHA)*$_2$ (**1c**)				
O-1–H-1···O-2^{ix}	0.97(2)	1.82(2)	2.734(2)	157(2)
O-2–H-2···O-1^{x}	0.73(2)	2.00(2)	2.722(2)	171(2)
C-1–H-1A···O-3^{xi}	1.05(2)	2.64(2)	3.534(3)	144(2)
C-1–H-1B···O-1^{xii}	0.98(2)	2.67(2)	3.474(3)	139(2)
C-3–H-3B···O-3^{xiii}	1.01(2)	2.51(2)	3.434(3)	152(2)

Symmetry codes: (*i*) $x, y+1, z$; (*ii*) $-x, -y+1, -z$; (*iii*) $-x+1, y-1/2, -z+1/2$; (*iv*) $-x+2, -y+1, -z+1$; (*v*) $-x+1, -y+2, -z+1$; (*vi*) $x, -y+3/2, z-1/2$; (*vii*) $x+1, y, z$; (*viii*) $x-1, y, z$, (*ix*) $-x, -y+1, -z+1$; (*x*) $x, -y+1/2, z-1/2$; (*xi*) $x, y-1, z$; (*xii*) $-x, -y, -z+1$; (*xiii*) $-x+1, y-1/2, -z+3/2$.

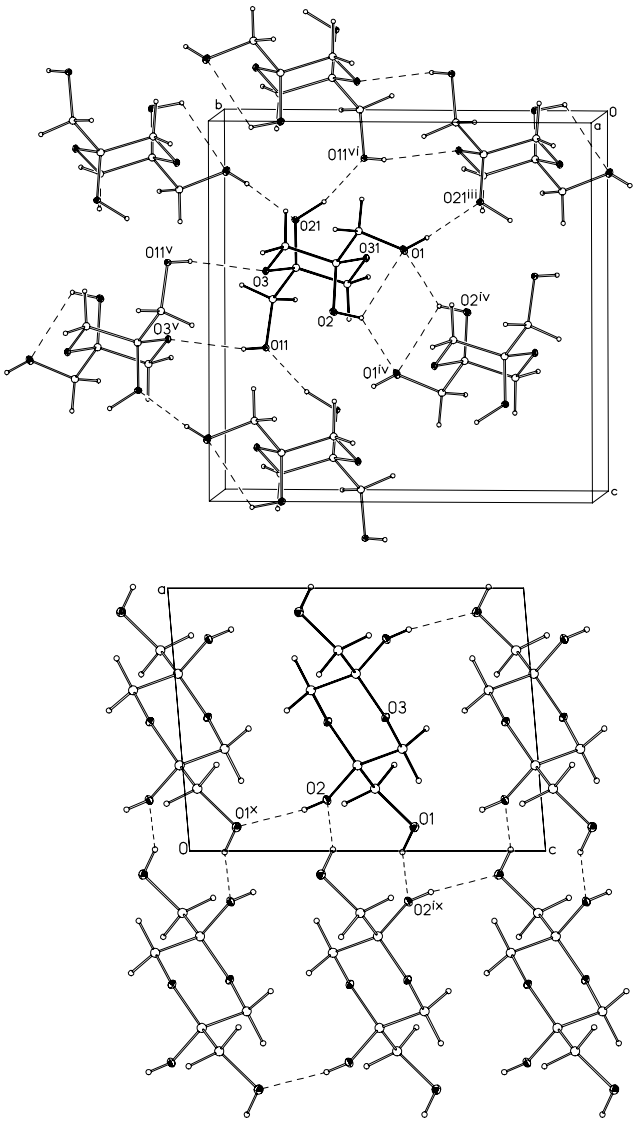


Figure 3. The crystal packing diagrams for **1b** (top) and **1c** (bottom). Dashed lines show the fragment of the three-dimensional O–H···O hydrogen bonds network. C–H···O contacts are omitted for clarity. (Symmetry codes are listed in Table 2).

2.2. Dihydroxyacetone monomer, DHA (2c) and its hydrated calcium chloride complexes, $CaCl_2(DHA)_2\cdot H_2O$ (2a), and $CaCl_2(DHA)\cdot 4H_2O$ (2b)

The crystals of **2a**—the calcium chloride complex of dihydroxyacetone monomer—are built up from Ca^{2+} and Cl^- ions, water molecules, and DHA monomer

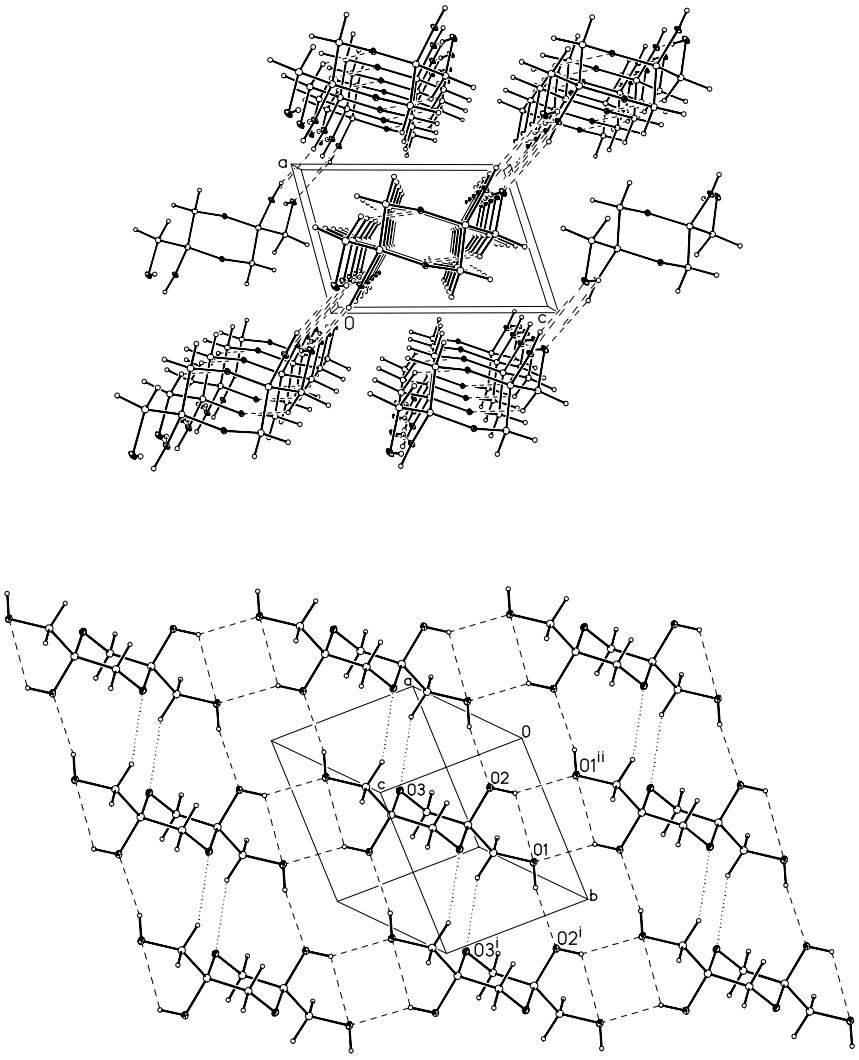


Figure 4. The crystal packing diagram for α-(DHA-dimer) **1a**, with layers formed by O–H···O (dashed lines) and C–H···O (dotted lines) hydrogen bonds shown (top) along with the arrangement of the molecules within the layer (bottom). (Symmetry codes are listed in Table 2).

molecules. Two Ca^{2+} ions are linked by two carbonyl oxygen bridges (from two symmetry-related DHA molecules) to form centrosymmetric dimer with Ca···Ca distance of 4.307(2) Å, as shown in Figure 5. The eight-coordinate polyhedra around the calcium cation is composed of three hydroxyl and three carbonyl O atoms (from three DHA molecules), one water molecule, and one chloride anion. Each metal cation is chelated by one of the DHA molecules (by its hydroxyl and carbonyl O atoms), while two other DHA molecules act as chelating as well as bridging ligands for both Ca^{2+} ions of the dimer. Calcium cation coordination-sphere data for **2a** and **2b** are listed in Table 3. Two crystallographically-independent DHA molecules are located on two, almost perpendicular planes. The first of them is built up from both Ca^{2+} ions and two symmetry-related DHA molecules, and the second one from calcium cations having Cl^- ions (Cl-1) coordinating to them, two other symmetry-related DHA, and water molecules. The planes intersect each other (with intersection on calcium cations) with an angle of 84.1(1)°.

The crystals of **2b**, the other calcium chloride complex of dihydroxyacetone monomer described here, are built up from two crystallographically-independent Ca^{2+} cations, coordinated to the DHA monomer and water molecules and noncoordinated Cl^- ions. Both calcium cations are involved in centrosymmetric dimers with Ca···Ca distances of 4.330(2) and 4.305(2) Å in the dimer built by Ca-1 and Ca-2, respectively. As observed in **2a**, and also in **2b**, symmetry-related metal centers are linked by two carbonyl oxygen bridges from two DHA molecules, which, with their hydroxyl groups coordinating to the distinct Ca^{2+} ions, act as chelating and bridging ligands simultaneously. Thus the eight-coordinate polyhedra of both metal centers in **2b** (Table 3) are composed of two hydroxyl and two carbonyl O atoms

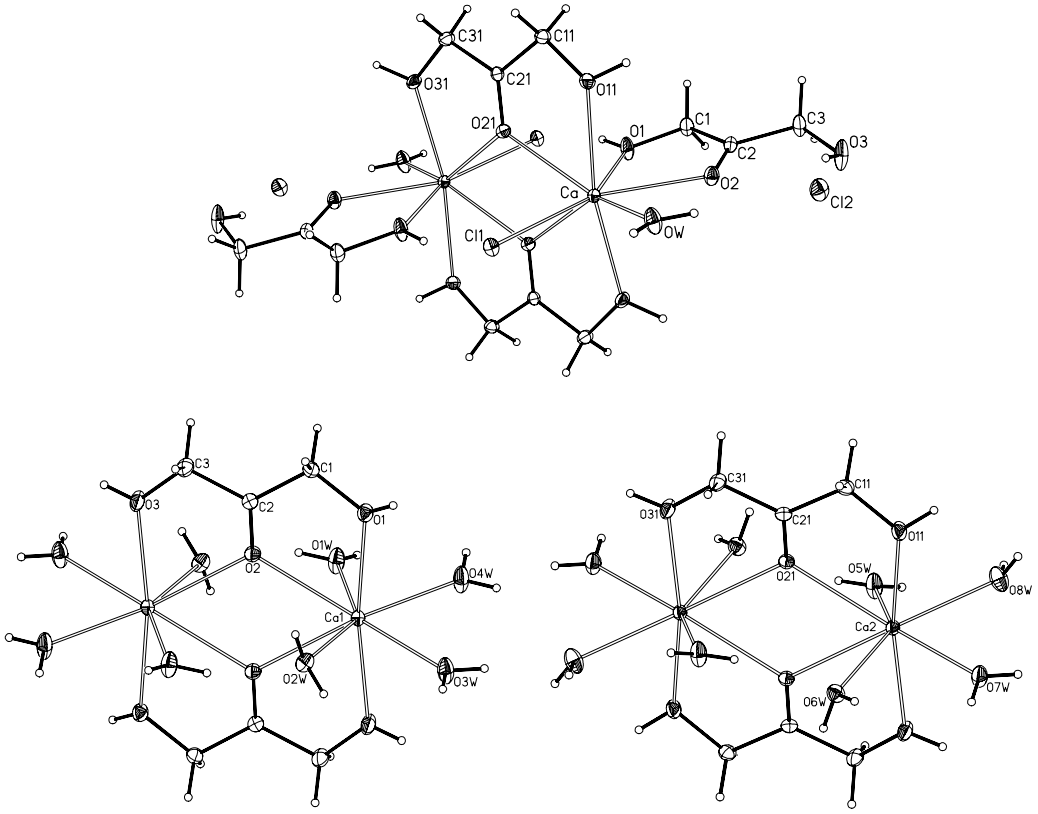


Figure 5. The hydrated dimeric calcium chloride complexes of dihydroxyacetone monomer: the complex cation along with noncoordinated Cl^- counterions in $CaCl_2(DHA)_2{\cdot}H_2O$ **2a** (top) and two crystallographically independent complex cations in $CaCl_2(DHA){\cdot}4H_2O$ **2b** (bottom).

Table 3. Coordination sphere of the Ca^{2+} ions in $CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**) and $CaCl_2(DHA){\cdot}4H_2O$ (**2b**), interatomic distances (Å) (standard deviations in parentheses)

$CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**)			
Ca–O-1	2.406(2)	Ca–Cl-1	2.7265(8)
Ca–O-11	2.442(2)	Ca–OW	2.383(1)
Ca–O-2	2.461(1)	Ca–O-21^i	2.562(2)
Ca–O-21	2.495(1)	Ca–O-31^i	2.369(1)
Ca$\cdots$Ca^i	4.307(2)		
$CaCl_2(DHA){\cdot}4H_2O$ (**2b**)			
Ca-1–O-1	2.475(1)	Ca-2–O-11	2.422(1)
Ca-1–O-2	2.523(1)	Ca-2–O-21	2.528(1)
Ca-1–O-2^i	2.583(1)	Ca-2–O-21^{ii}	2.538(1)
Ca-1–O-3^i	2.396(1)	Ca-2–O-31^{ii}	2.407(1)
Ca-1–O-1W	2.363(1)	Ca-2–O-5W	2.454(1)
Ca-1–O-2W	2.448(1)	Ca-2–O-6W	2.384(2)
Ca-1–O-3W	2.416(1)	Ca-2–O-7W	2.394(1)
Ca-1–O-4W	2.387(1)	Ca-2–O-8W	2.436(1)
Ca-1$\cdots$Ca-1^i	4.330(2)	Ca-2$\cdots$Ca-2^{ii}	4.305(2)

Symmetry codes: (*i*) $-x+1$, $-y+1$, $-z+1$; (*ii*) $-x+2$, $-y$, $-z$.

(from two symmetry-related DHA molecules), and are completed by four water molecules. It is noteworthy that in the dimer complex, DHA molecules and the Ca^{2+} ions are located on a plane. The plane intersects the other (built up from calcium cations and water molecules) with the angle of 87.7(1) and 88.5(1)° in the Ca-1 and Ca-2 dimers, respectively.

The overall molecular structure of the dihydroxyacetone monomer is similar in all three compounds **2a**,**b**, and **2c**. As shown in Figure 6, the molecules exist in an extended (*in-plane*) conformation with all of the non-H atoms lying in one plane and the hydroxyl H atoms being nearly in this plane. Both hydroxyl groups in all DHA molecules in **2a**–**2c** are then oriented *synperiplanar* (*sp*) in relation to the carbonyl O atom. The superimposing of the DHA molecular structures in **2a**–**2c**, shown in Figure 6 reveals the great similarity of the molecules, regardless of whether they are coordinated to the metal center or not. The relevant torsion angles for both crystallographically independent DHA molecules in the calcium chloride complexes **2a** and **2b** and for the DHA in **2b** are listed in Table 4.

All hydroxyl groups of the DHA molecules in **2a**–**c** are involved as both donors and acceptors, in medium strong, and weak O–H$\cdots$O hydrogen bonds. Additionally, in both calcium chloride complexes, **2a** and **2b**, water molecules, and chloride anions act in O–H$\cdots$Cl bonds to form three-dimensional network-linking complex dimers with each other. The structures are also stabilized by C–H$\cdots$Cl interdimeric interactions (Table 5). The two-dimensional network of O–H$\cdots$O hydrogen

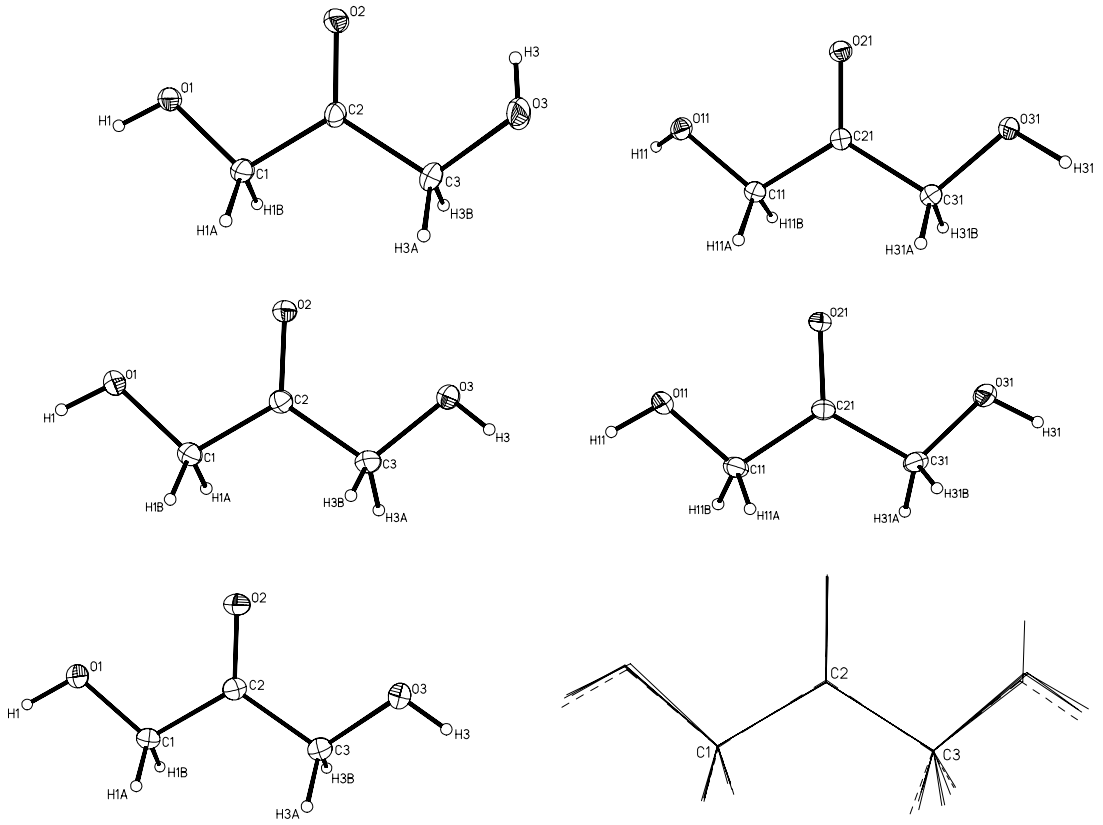


Figure 6. The molecular structure of two crystallographically independent DHA molecules in **2a** (top), in **2b** (in the middle) and DHA molecule in **2c** (bottom, left) (displacement ellipsoids at the 50% probability level for non-H atoms) and the comparison of their molecular structures (bottom, right); **2a**,**b**—solid lines, **2c**—dashed line. The common reference points are C-1, C-2, C-3 (or C-11, C-21, C-31).

Table 4. Conformation of the DHA molecules in **2a**–**c**, principal interatomic distances (Å), bond angles (°), and torsion angles (°) (standard deviations in parentheses)

	$CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**)	$CaCl_2(DHA){\cdot}4H_2O$ (**2b**)	(DHA) (**2c**)
O-1–C-1; O-11–C-11	1.408(2); 1.417(2)	1.426(2); 1.419(1)	1.408(1)
O-2–C-2; O-21–C-21	1.219(2); 1.221(2)	1.227(1); 1.227(1)	1.219(1)
O-3–C-3; O-31–C-31	1.407(2); 1.409(2)	1.415(2); 1.418(1)	1.410(1)
C-1–C-2; C-11–C-21	1.496(2); 1.500(2)	1.500(2); 1.497(1)	1.509(2)
C-2–C-3; C-21–C-31	1.499(2); 1.494(2)	1.499(2); 1.501(2)	1.510(2)
O-1–C-1–C-2; O-11–C-11–C-21	107.46(8); 109.65(7)	108.63(6); 107.94(6)	109.12(6)
O-2–C-2–C-1; O-21–C-21–C-11	121.00(8); 120.90(8)	121.17(7); 120.64(6)	122.34(7)
O-2–C-2–C-3; O-21–C-21–C-31	120.92(8); 120.38(8)	120.48(7); 121.12(6)	122.37(7)
C-1–C-2–C-3; C-11–C-21–C-31	118.09(8); 118.73(7)	118.35(6); 118.22(6)	115.29(6)
O-3–C-3–C-2; O-31–C-31–C-21	111.86(8); 108.64(7)	107.74(6); 108.59(6)	109.30(6)
O-1–C-1–C-2–O-2; O-11–C-11–C-21–O-21	1.0(2); −4.9(2)	−5.1(1); −7.3(1)	−0.1(1)
O-1–C-1–C-2–C-3; O-11–C-11–C-21–C-31	−179.6(2); 175.3(1)	175.1(1); 171.5(1)	−180.0(1)
O-2–C-2–C-3–O-3; O-21–C-21–C-31–O-31	8.8(2); 0.3(2)	−8.6(1); −9.1(1)	10.4(1)
C-1–C-2–C-3–O-3; C-11–C-21–C-31–O-31	−170.7(2); −180.0(1)	171.2(1); 172.1(1)	−169.7(1)

bonding in **2c** links adjacent DHA molecules in layers (Fig. 7), which are linked each other by C–H···O intermolecular, interlayer contacts. Both hydroxyl groups act as bifurcated donors in O–H···O interactions with the hydroxyl and carbonyl group from the adjacent DHA molecule and, simultaneously, as an acceptor of such contact from another symmetry-related DHA molecule. Thus every four molecules form a cyclic hydrogen-bonded structure, as shown in Figure 7 (left).

2.3. Dihydroxyacetone dimethyl acetal $(MeO)_2$DHA (3)

The molecular structure of the dimethyl acetal of the dihydroxyacetone is shown in Figure 8 and principal bond lengths, bond angles, and torsion angles are listed

Table 5. Geometry of proposed hydrogen bonds and close C–H···X contacts (X = O or Cl) for **2a**–**c**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
$CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**)				
O-1–H-1···Cl-1^{i}	0.82(2)	2.21(2)	3.011(1)	165(2)
O-3–H-3···Cl-2	0.77(2)	2.37(2)	3.095(2)	158(2)
O-11–H-11···Cl-2^{ii}	0.86(2)	2.19(2)	3.035(1)	166(2)
O-31–H-31···O-3^{iii}	0.91(2)	1.71(2)	2.610(2)	174(2)
OW–H-1W···Cl-2	0.80(2)	2.41(2)	3.214(2)	177(2)
OW–H-2W···Cl-2^{iv}	0.85(2)	2.46(2)	3.287(2)	163(2)
C-1–H-1A···Cl-2^{v}	1.02(2)	3.00(2)	3.939(2)	154(2)
C-1–H-1B···Cl-1^{vi}	0.93(2)	2.98(2)	3.690(2)	134(1)
C-3–H-3A···O-2^{v}	0.98(2)	2.58(2)	3.432(2)	145(2)
C-3–H-3B···Cl-2^{ii}	0.96(2)	3.08(2)	3.678(2)	123(2)
C-11–H-11A···Cl-1^{vii}	0.97(2)	3.01(2)	3.705(2)	130(2)
C-11–H-11B···Cl-1^{vi}	0.94(2)	2.73(2)	3.533(2)	144(2)
C-31–H-31A···Cl-1^{vii}	0.92(2)	2.78(2)	3.470(2)	132(2)
C-31–H-31B···Cl-1^{vi}	0.96(2)	2.99(2)	3.729(2)	135(1)
$CaCl_2(DHA){\cdot}4H_2O$ (**2b**)				
O-1–H-1···Cl-3	0.82(2)	2.20(2)	3.009(2)	170(2)
O-3–H-3···Cl-1	0.78(2)	2.24(2)	3.014(2)	177(2)
O-11–H-11···Cl-3^{i}	0.82(2)	2.27(2)	3.068(1)	165(2)
O-31–H-31···Cl-4	0.82(2)	2.25(2)	3.068(2)	178(2)
O-1W–H-1W···Cl-3^{viii}	0.78(2)	2.39(2)	3.168(2)	179(2)
O-1W–H-2W···O-2W^{i}	0.80(2)	2.07(2)	2.836(2)	162(2)
O-2W–H-3W···Cl-4^{ix}	0.84(2)	2.39(2)	3.175(2)	157(2)
O-2W–H-4W···Cl-2	0.81(2)	2.30(2)	3.104(1)	173(2)
O-3W–H-5W···Cl-4^{ix}	0.79(2)	2.39(2)	3.151(2)	163(2)
O-3W–H-6W···Cl-1^{x}	0.79(2)	2.51(2)	3.267(2)	160(2)
O-4W–H-7W···O-1^{viii}	0.72(2)	2.28(2)	2.940(2)	154(2)
O-4W–H-8W···Cl-1^{x}	0.80(2)	2.31(2)	3.109(2)	174(2)
O-5W–H-9W···Cl-4^{xi}	0.80(2)	2.37(2)	3.162(2)	169(2)
O-5W–H-10W···Cl-2^{xii}	0.80(2)	2.49(2)	3.227(2)	154(2)
O-6W–H-11W···Cl-1^{xiii}	0.80(2)	2.40(2)	3.160(2)	158(2)
O-6W–H-12W···O-5W^{xiv}	0.79(2)	2.15(2)	2.856(2)	148(2)
O-7W–H-13W···Cl-2^{xii}	0.82(2)	2.37(2)	3.186(2)	171(2)
O-7W–H-14W···Cl-2^{xiii}	0.78(2)	2.43(2)	3.180(2)	162(2)
O-8W–H-17W···Cl-1^{xiii}	0.79(2)	2.47(2)	3.230(2)	161(2)
O-8W–H-18W···Cl-3^{i}	0.78(2)	2.51(2)	3.266(2)	163(2)
C-1–H-1A···Cl-1^{vii}	1.00(2)	3.10(2)	3.859(2)	134(2)
C-1–H-1B···Cl-2	0.97(2)	2.77(2)	3.395(2)	123(1)
C-3–H-3B···Cl-4^{xv}	0.97(2)	2.96(2)	3.516(2)	118(1)
C-11–H-11A···Cl-3^{xii}	0.91(2)	3.02(2)	3.640(2)	127(1)
C-11–H-11B···Cl-2^{i}	0.95(2)	2.86(2)	3.679(2)	145(1)
C-31–H-31B···Cl-2^{xvi}	0.95(2)	3.11(2)	3.672(2)	120(2)
DHA (**2c**)				
O-1–H-1···O-3^{xvii}	0.87(2)	1.91(2)	2.730(2)	155(2)
O-1–H-1···O-2^{xvii}	0.87(2)	2.56(2)	3.227(2)	134(2)
O-3–H-3···O-1^{xviii}	0.80(2)	2.10(2)	2.743(1)	137(2)
O-3–H-3···O-2^{xviii}	0.80(2)	2.35(2)	3.073(1)	149(2)
C-1–H-1B···O-3^{xix}	0.99(2)	2.65(2)	3.602(2)	162(1)

Symmetry codes: (*i*) $-x+1, -y+1, -z+1$; (*ii*) $-x+1/2, y+1/2, -z+3/2$; (*iii*) $x-1/2, -y+3/2, z-1/2$; (*iv*) $-x+1/2, y-1/2, -z+3/2$; (*v*) $-x+3/2, y+1/2, -z+3/2$; (*vi*) $x, y+1, z$; (*vii*) $-x, -y+1, -z+1$; (*viii*) $-x+1, -y+2, -z+1$; (*ix*) $x, y, z+1$ (*x*); $x+1, y+1, z$; (*xi*) $x, y-1, z$; (*xii*) $x, y-1, z-1$; (*xiii*) $-x+1, -y, -z+1$; (*xiv*) $-x+2, -y, -z$; (*xv*) $x-1, y, z+1$; (*xvi*) $x, y, z-1$; (*xvii*) $x+1, -y+1/2, z+1/2$; (*xviii*) $-x, y+1/2, -z+1/2$; (*xix*) $x+1, y, z$.

in Table 6. As may be seen from Figure 8, the conformation of the $(MeO)_2$DHA molecule may be described as deformed swastika like. When looking as shown in Figure 8 (right), one may see two zig-zag chains: *Z*-shaped O-1–C-1–C-2–C-3–O-3 and *S*-shaped C-4–O-21–C-2–O-22–C-5 intersecting each other at C-2 to form eight-shaped structure. The probable reason for the adopting such conformation by the molecule is the anomeric effect, which plays an important role in carbohydrate chemistry. It is reflected in bond angles with their vertex on C-2. As shown in Table 6, two of these angles: C-1–C-2–O-21 and C-3–C-2–O-22 are much smaller than the others O–C–O, O–C–C, and C–C–C valence angles.

The crystal structure of dihydroxyacetone dimethyl acetal is stabilized by an O–H···O and C–H···O hydrogen-bonding system, in which both hydroxyl groups and ether O atoms are involved (Table 7). Each molecule of $(MeO)_2$DHA is joined with another, symmetry-related, by its hydroxyl groups (one as donor and one as acceptor) to form *head-to-head* molecular pairs. Additionally it is involved in bifurcated O–H···O hydrogen bonds with another *head-to-head* pair of molecules to form double layers parallel to the (1 0 1) plane. Within the layers, shown in Figure 9, several intermolecular C–H···O interactions are formed. In addition, there are also C-5–H-5B···O-22^{iv} contacts linking adjacent layers (symmetry codes are listed in Table 7).

3. Experimental

3.1. Preparation of crystals

The tear-shape, colorless (with a tendency to twinning) crystals of the α form of dihydroxyacetone dimer **1a** were obtained by recrystallization of commercially available (Aldrich) dihydroxyacetone from aqueous solution at room temperature. The thin plates of form β (**1b**) were grown in analogous way by the use of 2-propanol. The very thin, colorless tear-shape plates of the next DHA-dimer polymorph–γ-(DHA-dimer) (**1c**) were obtained by a slowed down lyophilization process. The large, colorless blocks of **2a** and **2b** were obtained by slow evaporation of an aqueous solution containing a 1:1 and 1:2, respectively, molar ratio mixture of commercial DHA dimer (previously dissolved in water) and $CaCl_2{\cdot}6H_2O$ at 4 °C. Lyophilization of a water solution of commercially DHA (130 mg/mL) after 24 h at room temperature gave small and poor quality thin plates of **2c**. Further, room temperature recrystallization from EtOH (or another alcohol such as 2-PrOH) gave well defined, rather thick plates. This process had to be taken under nitrogen flow, because of the hygroscopicity of the DHA monomer crystals (**2c**). Finally, the dihydroxyacetone dimethyl acetal (**3**) was prepared by using our

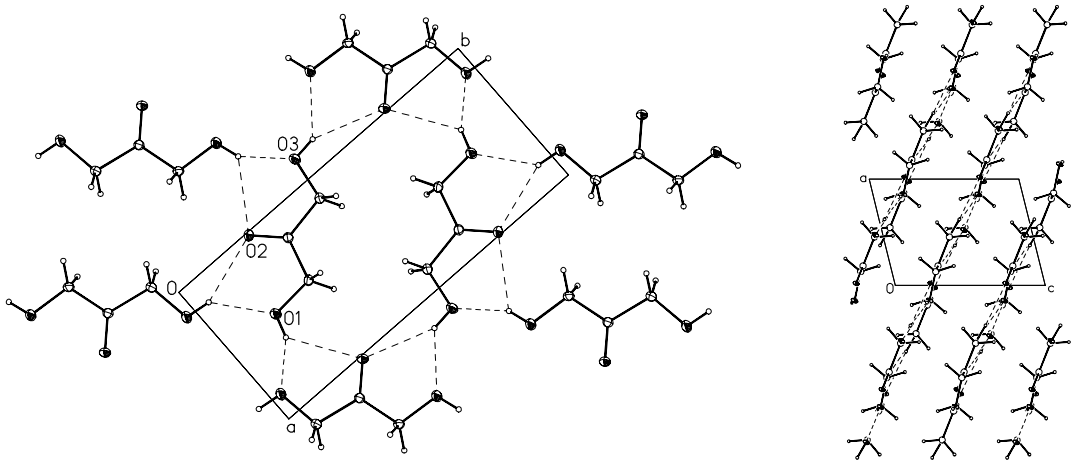


Figure 7. Layers formed by two-dimensional O–H···O hydrogen bonds network in **2c**. View along *c* (left) and *b* (right) axis.

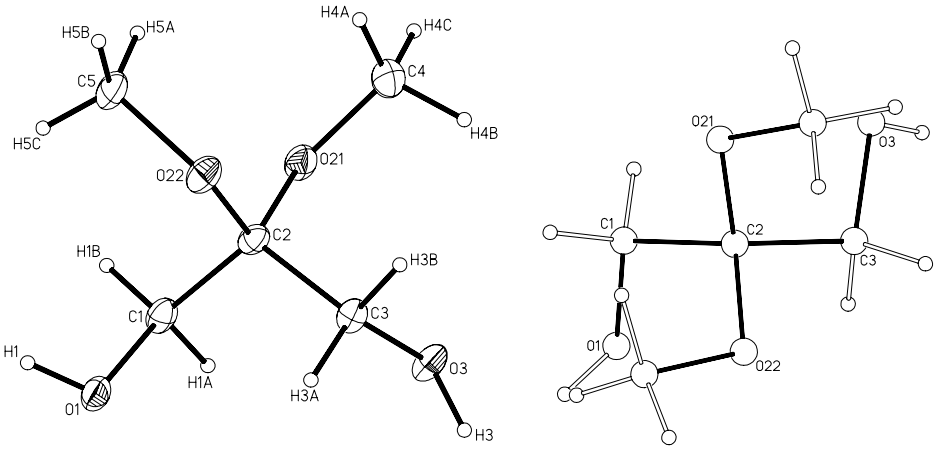


Figure 8. The molecular structure with the atom-numbering scheme for dihydroxyacetone dimethyl acetal molecule in **3** (left—displacement ellipsoids at the 30% probability level for non-H atoms).

Table 6. Principal interatomic distances (Å), bond angles (°) and torsion angles (°) in **3** (standard deviations in parentheses)

Bond/angle		Torsion angle	
O-1–C-1	1.431(2)	C-4–O-21–C-2–O22	55.7(2)
O-21–C-2	1.415(2)	C-4–O-21–C-2–C-1	178.5(2)
O-21–C-4	1.427(3)	C-4–O-21–C-2–C-3	−60.3(2)
O-22–C-2	1.416(2)	C-5–O-22–C-2–O-21	56.2(2)
O-22–C-5	1.431(2)	C-5–O-22–C-2–C-1	−60.9(2)
O-3–C-3	1.429(2)	C-5–O-22–C-2–C-3	177.2(2)
C-1–C-2	1.527(3)	O-1–C-1–C-2–O-21	−175.1(2)
C-2–C-3	1.530(2)	O-1–C-1–C-2–O-22	−53.2(2)
O-21–C-2–O-22	112.2(2)	O-1–C-1–C-2–C-3	63.9(2)
O-21–C-2–C-1	103.7(2)	O-21–C-2–C-3–O-3	−44.4(2)
O-22–C-2–C-1	113.5(2)	O-22–C-2–C-3–O-3	−165.5(2)
O-21–C-2–C-3	112.0(2)	C-1–C-2–C-3–O-3	71.7(2)
O-22–C-2–C-3	103.6(2)		
C-1–C-2–C-3	112.2(2)		
O-3–C-3–C-2	109.4(2)		

modification of the method of Ferroni et al.[11] namely, by reacting of DHA with 2,2-dimethoxypropane (DMP) in absolute MeOH in the presence of catalytic amounts of *p*-toluenesulfonic acid (Scheme 1). Colorless, platelike, very air-sensitive crystals of **3** grew in the receiver during the vacuum distillation of the product.

3.2. Crystal structure determination

The crystallographic measurements of the **1a**,**1b**, and **2a** crystals were performed on a Kuma KM4 automated four-circle diffractometer using graphite-monochromatized Cu-K_α (for **1a** and **1b**) and Mo-K_α (for **2a**) radiation at 295(2), 294(2), and 100(2) K, respectively. During the experiments, the stability of intensities was monitored by measurement of three standards every 100

Table 7. Geometry of proposed hydrogen bonds and close C–H···O contacts for **3**

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O-1–H-1···O-3^{i}	0.85(3)	2.01(3)	2.839(2)	166(3)
O-1–H-1···O-21^{i}	0.85(3)	2.63(3)	3.136(2)	120(2)
O-3–H-3···O-1^{ii}	0.92(3)	1.81(3)	2.719(2)	173(2)
C-1–H-1B···O-21^{iii}	0.97(2)	2.52(2)	3.420(3)	156(2)
C-5–H-5B···O-22^{iv}	0.95(3)	2.67(2)	3.549(3)	154(2)
C-5–H-5C···O-3^{i}	0.90(3)	2.63(3)	3.509(3)	166(2)

Symmetry codes: (*i*) $-x+3/2$, $y-1/2$, $-z+3/2$; (*ii*) $-x+3/2$, $-y+3/2$, $-z+2$; (*iii*) $-x+3/2$, $-y+3/2$, $-z+1$; (*iv*) $-x+1$, $-y+1$, $-z+1$.

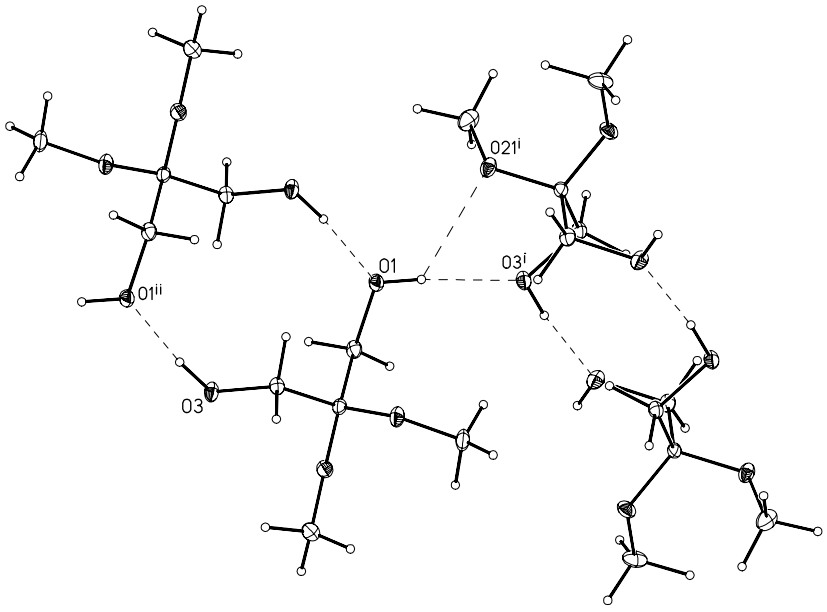


Figure 9. Fragment of double layer formed by O–H···O bonds in **3**.

Table 8. Experimental data for **1a**–**c**

	α-(DHA-dimer) (**1a**)	β-(DHA-dimer) (**1b**)	γ-(DHA-dimer) (**1c**)
Crystal data			
Empirical formula	$C_6H_{12}O_6$	$C_6H_{12}O_6$	$C_6H_{12}O_6$
Formula weight (g mol^{-1})	180.16	180.16	180.16
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	5.499(3)	7.015(6)	6.831(5)
b (Å)	5.528(3)	10.513(8)	6.274(4)
c (Å)	7.170(4)	10.543(6)	9.194(6)
α (°)	95.12(4)		
β (°)	102.43(4)	94.25(6)	94.79(6)
γ (°)	116.22(4)		
V (Å^3)	186.7(2)	775.4(10)	392.7(5)
Z	1	4	2
D_{calc} (g cm^{-3})	1.603	1.543	1.524
μ (mm^{-1})	1.270	1.223	0.138
F (0 0 0)	96	384	192
Crystal size (mm)	0.2 × 0.2 × 0.1	0.35 × 0.20 × 0.02	0.20 × 0.08 × 0.02
Crystal form	Tear-like plate	Plate	Tear-like plate
Crystal color	Colorless	Colorless	Colorless
Data collection			
Diffractometer	Kuma KM4	Kuma KM4	Kuma KM4CCD
Monochromator	Graphite	Graphite	Graphite

Table 8 (*continued*)

	α-(DHA-dimer) (**1a**)	β-(DHA-dimer) (**1b**)	γ-(DHA-dimer) (**1c**)
Radiation type	Cu-K_α	Cu-K_α	Mo-K_α
Wavelength, λ (Å)	1.5418	1.5418	0.71073
T (K)	295(2)	294(2)	100(2)
θ Range (°)	6.47–80.53	5.95–80.90	3.94–29.99
Indexs range	$-7 \leqslant h \leqslant 6$	$-8 \leqslant h \leqslant 8$	$-9 \leqslant h \leqslant 6$
	$-7 \leqslant k \leqslant 7$	$-13 \leqslant k \leqslant 13$	$-8 \leqslant k \leqslant 8$
	$-9 \leqslant l \leqslant 9$	$-13 \leqslant l \leqslant 13$	$-12 \leqslant l \leqslant 12$
Absorption correction	Empirical	Empirical	—
T_{min}/T_{max}	0.485/0.834	0.474/0.830	—
Measured reflections	1461	3467	3484
Independent reflections	758	1667	1101
Observed refl. ($I > 2\sigma(I)$)	671	1129	524
R_{int}	0.0231	0.0388	0.0786
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.21/−0.16	0.22/−0.14	0.27/−0.19
Refinement			
Refinement on	F^2	F^2	F^2
Data/restraints/parameters	758/0/80	1667/0/157	1101/0/78
R ($F_o^2 > 2\sigma(F_o^2)$)	$R1 = 0.0298$	$R1 = 0.0338$	$R1 = 0.0572$
	$wR2 = 0.0719$	$wR2 = 0.0761$	$wR2 = 0.0372$
R (all data)	$R1 = 0.0355$	$R1 = 0.0659$	$R1 = 0.1665$
	$wR2 = 0.0749$	$wR2 = 0.0881$	$wR2 = 0.0464$
GooF = S	1.088	0.997	0.949
Weighting parameter a	0.0283	0.0407	0.0
Weighting parameter b	0.0554	0.1146	0.0

$W = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

reflections. For **1c**, **2b**,**c**, and **3**, the data collection was carried out at 100(2) K with a Kuma KM4CCD diffractometer with the Mo-K_α radiation type, using the Oxford Cryosystem cooler, as in the case of **2a**. A summary of the conditions for the data collection and the structure refinement parameters are given in Tables 8 and 9. The data for **1a** and **1b** were empirically corrected for absorption using the DIFABS program,[13] for **2a** with the Gaussian method using XPREP program from the SHELXTL package,[14] and for **2b** numerically with the use of CRYSALIS RED 1.171, the KM4CCD software.[15] The structures of all crystals were solved by direct methods using the SHELXS-97 program[16] and refined by a full-matrix least-squares technique using SHELXL-97,[17] with anisotropic thermal parameters for non-H atoms. The H atoms were found in difference-Fourier maps and were refined isotropically except for H-1A in **1c**, which was refined with U_{iso} equal

Table 9. Experimental data for **2a**–**3**

	$CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**)	$CaCl_2(DHA){\cdot}4H_2O$ (**2b**)	DHA (**2c**)	$(MeO)_2DHA$ (**3**)
Crystal data				
Empirical formula	$C_6H_{14}CaCl_2O_7$	$C_3H_{14}CaCl_2O_7$	$C_3H_6O_3$	$C_5H_{12}O_4$
Formula weight (g mol^{-1})	309.15	273.12	90.08	136.15
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	7.309(3)	9.029(2)	5.151(2)	15.937(7)
b (Å)	7.344(3)	9.087(2)	11.057(3)	10.379(5)
c (Å)	22.831(6)	14.054(3)	7.045(2)	9.169(5)
α (°)		90.41(3)		
β (°)	92.29(3)	100.34(3)	103.78(3)	114.37(6)
γ (°)		93.27(3)		
V (Å^3)	1224.5(8)	1132.3(4)	389.7(2)	1381.5(12)
Z	4	4	4	8
D_{calc} (g cm^{-3})	1.677	1.602	1.535	1.309
μ (mm^{-1})	0.964	1.030	0.139	0.113
F (0 0 0)	640	568	192	592
Crystal size (mm)	0.7 × 0.35 × 0.2	0.36 × 0.36 × 0.36	0.4 × 0.2 × 0.15	0.6 × 0.5 × 0.1
Crystal form	Parallelepiped	Parallelepiped	Plate	Plate
Crystal color	Colorless	Colorless	Colorless	Colorless

(*continued on next page*)

Table 9 (*continued*)

	$CaCl_2(DHA)_2{\cdot}H_2O$ (**2a**)	$CaCl_2(DHA){\cdot}4H_2O$ (**2b**)	DHA (**2c**)	$(MeO)_2DHA$ (**3**)
Data collection				
Diffractometer	Kuma KM4	Kuma KM4CCD	Kuma KM4CCD	Kuma KM4CCD
Monochromator	Graphite	Graphite	Graphite	Graphite
Radiation type	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Wavelength, λ (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	100(2)	100(2)	100(2)	100(2)
Range (°)	2.89–35.09	3.28–37.47	3.50–36.21	3.82–28.49
Indexs range	$-2 \leqslant h \leqslant 11$	$-15 \leqslant h \leqslant 13$	$-8 \leqslant h \leqslant 7$	$-21 \leqslant h \leqslant 17$
	$0 \leqslant k \leqslant 11$	$-15 \leqslant k \leqslant 15$	$-17 \leqslant k \leqslant 18$	$-13 \leqslant k \leqslant 13$
	$-36 \leqslant l \leqslant 36$	$-23 \leqslant l \leqslant 23$	$-11 \leqslant l \leqslant 10$	$-12 \leqslant l \leqslant 12$
Absorption correction	Gaussian	Numerical	—	—
T_{min}/T_{max}	0.719/0.826	0.736/0.782	—	—
Measured reflections	6639	20296	5863	4253
Independent reflections	5289	10298	1722	1618
Observed refl. ($I > 2\sigma(I)$)	4173	9014	1450	1179
R_{int}	0.0219	0.0228	0.0293	0.0717
$\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.63/−0.46	0.60/−0.30	0.60/−0.22	0.28/−0.28
Refinement				
Refinement on	F^2	F^2	F^2	F^2
Data/restraints/parameters	5289/0/202	10298/ 0/352	1722/0/79	1618/0/130
R ($F_o^2 > 2\sigma(F_o^2)$)	$R1 = 0.0230$	$R1 = 0.0239$	$R1 = 0.0418$	$R1 = 0.0573$
	$wR2 = 0.0621$	$wR2 = 0.0577$	$wR2 = 0.1103$	$wR2 = 0.1341$
R (all data)	$R1 = 0.0413$	$R1 = 0.0292$	$R1 = 0.0523$	$R1 = 0.0828$
	$wR2 = 0.0670$	$wR2 = 0.0593$	$wR2 = 0.1158$	$wR2 = 0.1519$
GooF = S	1.070	1.051	1.104	1.051
Weighting parameter a	0.0357	0.0341	0.0686	0.0826
Weighting parameter b	0.1411	0.1335	0.0257	0.0

$W = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

to the C-1 atom. One of the chloride ions in **2b** is slightly disordered into the Cl-1 and Cl-01 positions, with the occupancy factors being equal to 0.964(5) and 0.036(5), respectively. Due to the low occupation of Cl-01, only the Cl-1 position was discussed. For **1a** and **2a** the extinction was also refined with the final extinction coefficients amounting to 0.013(5) and 0.0097(10), respectively. The scattering factors were taken from Ref. 18. All figures were made using an XP program.[19]

4. Supplementary material

The Cambridge Crystallographic Data Center (CCDC) has the supplementary crystallographic data for this paper: (**1a**) (CCDC 231358), (**1b**) (CCDC 231359), (**1c**) (CCDC 231360), (**2a**) (CCDC 231361), (**2b**) (CCDC 231362), (**2c**) (CCDC 231363), and (**3**) (CCDC 231364).

These data may be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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