A Supramolecular Three-Dimensional Hydrogen-Bonded Network with Potential Application in Crystal Engineering Paradigms

Jack D. Dunitz*

Abstract: The combination of carboxylic acid groups separated by linear spacers with linking water molecules is shown to yield a three-dimensional self-assembling hydrogen-bonding system that is practically invariant with respect to the length of the spacer. The structure-directing properties of such supramolecular synthons are discussed in terms of their encoded stereochemical and functional information.

Keywords: aggregations · chiral selection · hydrogen bonding · molecular recognition · molecular switches · self-assembly · structure-directing interactions · supramolecular chemistry · synthons

Introduction

Our ongoing interest in the design of supramolecular systems based on simple synthons with pronounced hydrogen-bonding capabilities and associated structure-directing properties has led us to reexamine the now classic crystal structure of oxalic acid dihydrate[1] (**1**) with a view to systematic variation of the basic molecular framework. The underlying strategical concept behind our work consists in preserving as far as possible the geometric relationship between the two carboxylic acid moieties of the oxalic acid molecule while varying the distance between them. To achieve this goal we have elected to introduce one or more acetylenic units as linear spacers, with the prospect of attaining the desired target geometry with only modest synthetic effort.

Results and Discussion

In this paper we report that our simple planning strategy has elicited the intended result. Acetylene dicarboxylic acid dihydrate (**2**) and diacetylene dicarboxylic acid dihydrate (**3**) have been successfully prepared and obtained as crystalline samples amenable to X-ray analysis.[2] In accord with our planning and as we had envisaged, almost exactly the same structural motif is shown to occur in the crystals of **1** and **2**, and, with minor space-group variations noted later, also in **3**.[3] In all three structures, the two molecules of water and the carboxylic acid groups at each end of the variable carbon chains are common factors which closely determine the manner in which the crystals are constructed. The observed motif is self-assembled from mutually complementary partners possessing encoded stereochemical and functional information that is read by the recognition and selection processes responsible for crystal nucleation and subsequent growth.

This constancy in the hydrogen-bonding pattern in our three structures augurs well for the crystal engineering design potential of further nanosystems where common features of a system of hydrogen-bond donors and acceptors are maintained by suitable synthetic directives, while allowing variability by means of appropriate mutations of the connecting carbon framework.

The common features of the three crystal structures are visible in Figure 1. The protonated oxygen atom of each carboxyl group acts as strong hydrogen bond donor to a water molecule (O···O, 250–256 pm), which, in turn, is engaged in two somewhat longer and presumably weaker hydrogen bonds to carbonyl oxygen atoms of two different diacid molecules (O···O, 282–290 pm). The linear diacid structural units are thus associated into a system of interconnected layers by an infinite three-dimensional network, the links of which consist of: 1) hydrogen-bonded helices running around the 2_1 screw axes, each complete turn comprising two carboxyl groups and two water molecules; 2) hydrogen-bonded quadrilaterals formed by pairs of centrosymmetrically related water molecules and correspondingly related pairs of carbonyl oxygens. In the figure, the individual layers appear in projection onto the plane as chains and the helices as 8-membered rings. It is noteworthy that each helix of a given sense of chirality is surrounded by four neighboring ones with precisely the opposite sense of chirality, this relationship being a consequence of the presence of the inversion centres that ornament the entire pattern in such a beautifully decorative manner.

---

[*] Prof. J. D. Dunitz
Organic Chemistry Laboratory
Swiss Federal Institute of Technology
ETH-Zentrum, CH-8092 Zurich (Switzerland)
E-mail: dunitz@org.chem.ethz.ch

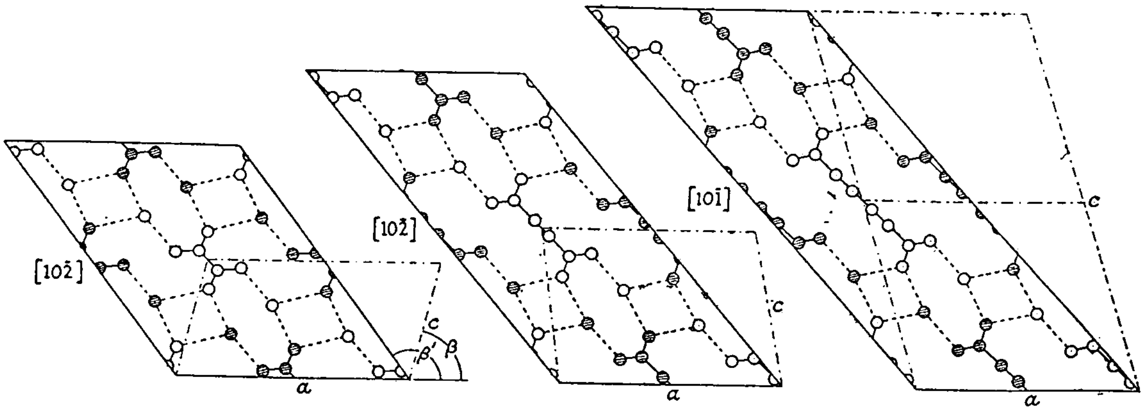

Figure 1. Unit cells and atomic arrangements in **1**, **2** and **3**. The shaded atoms differ from the corresponding unshaded ones by a reflection across the projection plane (010) and a translation of *b*/2. Notice the essential invariance of the hydrogen-bonded packing pattern as the carbon chain spacer is lengthened.

While the projections of the three crystal structures depicted in the figure appear to show essentially the same motif, there is a subtle but none the less important difference between them. Structures **1** and **2** belong to the same space group $P2_1/a$. The unit cell contents comprise two molecules of dihydrate, and space-group symmetry then requires that the molecular centers are located on a set of crystallographic inversion centers. The carboxyl groups at either end of the diacid molecules are therefore required to lie in parallel planes. In fact, the molecules of oxalic acid and of acetylene dicarboxylic acid in our dihydrate crystals are strictly planar, with the implication of a significant degree of delocalization of the 3-center–4-electron π systems of the separated carboxyl groups.

Structure **3** chooses to crystallize in a different space group, $I2/c$ (a variant of the standard orientation $C2/c$). With four molecules of dihydrate in the doubled unit cell, space-group symmetry requirements could be fulfilled with the molecular centers located either on crystallographic inversion centers or twofold rotation axes. The X-ray analysis shows unambiguously that the second alternative is adopted. In contrast to the other two diacid molecules, the molecule of diacetylene dicarboxylic acid is not planar. Instead, the two carboxyl groups are mutually rotated about the long molecular axis to produce an angle of 57° between them. As a result, and in contrast to the planar achiral molecules of oxalic acid and acetylene dicarboxylic acid, each diacetylene dicarboxylic acid in the dihydrate crystal adopts a chiral conformation, and it is remarkable that every molecule within a given crystal layer (projecting as a chain in the figure) possesses the same sense of chirality. The layers are thus *homochiral* entities, and successive layers, related by inversion centers, must have opposite sense of chirality. At a crucial stage in the self-assembly process associated with formation of the crystals, an essential recognition step imposes chirality on achiral precursor molecules and stamps each such molecule with a given sense of chirality that enables it to be incorporated in the growing layer. Since successive layers have opposite senses of chirality, the growing crystal can be regarded as a molecular switching device, the switch involving mutual rotation of the carboxylic acid groups at either end of the molecules.

In spite of the changes of space group and molecular symmetry within this set of hydrogen-bonded crystal structures, the stereochemical and functional information encoded in the carboxylic acid groups at each end of the variable carbon chains in these rodlike molecules imposes structural imperatives on the recognition and selection processes involved in crystal nucleation and subsequent growth, resulting in closely related crystal structures characterized by important and essential common factors. We are employing the same strategy to develop other supramolecular frameworks that should produce interesting new and novel systems of potential usefulness in molecular switching devices, nonlinear optics, and liquid crystalline systems.

Received: December 23, 1997 [L959]

---

[1] J. M. Robertson, I. Woodward, *J. Chem. Soc.* **1936**, 1817; R. Brill, C. Hermann, C. Peters, *Ann. Physik* **1942**, *42*, 357; Y. Wang, R. H. Blessing, F. K. Ross, P. Coppens, *Acta Crystallogr.* **1976**, *B32*, 572; P. Coppens, M. S. Lehmann, *Acta Crytsallogr.* **1976**, *B32*, 1777.

[2] See also: J. D. Dunitz, J. Monteath Robertson, *J. Chem. Soc.* **1947**, 142–148; *idem*, *ibid.* **1947**, 148–154; *idem*, *ibid.* **1947**, 1145–1156.

[3] Crystal data for **1**, $C_2H_2O_4 \cdot 2H_2O$; $M = 126.07$; monoclinic, space group $P2_1/a$; $a = 1188$, $b = 360$, $c = 612$ pm, $\beta = 76.5°$, $V = 0.2545$ nm^3; $Z = 2$; $\rho_{\text{calcd}} = 1.65$ Mg m^{-3}. Crystal data for **2**, $C_4H_2O_4 \cdot 2H_2O$; $M = 150.09$; monoclinic, space group $P2_1/a$; $a = 1105(3)$, $b = 386(1)$, $c = 798(2)$ pm, $\beta = 98.0(3)°$, $V = 0.3371$ nm^3; $Z = 2$; $\rho_{\text{calcd}} = 1.48$ Mg m^{-3}; $\mu(\text{Cu}_{K\alpha}) = 14.5$ cm^{-1}. Crystal data for **3**, $C_6H_2O_4 \cdot 2H_2O$; $M = 174.11$; monoclinic, space group $I2/c$; $a = 1115$, $b = 375$, $c = 2018$ pm, $\beta = 107.0°$, $V = 0.8069$ nm^3; $Z = 4$; $\rho_{\text{calcd}} = 1.43$ Mg m^{-3}; $\mu(\text{Cu}_{K\alpha}) = 13.4$ cm^{-1}. 0*kl*, *h*0*l* and *hk*0 reflections. Structure determination for **2** and **3** by TRIAL, refinement by iterated cycles of Fourier projections and SF calculations with empirical scattering factors.