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A hand-twisted helical crystal based solely on hydrogen bonding†

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A hand twistable hydrogen bonded two-dimensional plastic crystal, 4-pyridinyl 4-nitrobenzoate hydrate, is obtained from a brittle precursor using a retrosynthetic design strategy based on molecular/supramolecular equivalence.

Crystal engineering, the designed synthesis of functional molecular solids,[1] has gained increasing scope and generality owing to the significant progress in obtaining crystal design strategies from the analysis of large amounts of crystal structure data, generally through the application of the supramolecular synthon concept.[2] In previous publications, we characterized these phases of development as first and second generation crystal engineering.[3] The subject has now matured into property engineering, realizing that the same property may be realized for structures that may be similar or even different from a benchmark starting point. This recent trend signifies third generation crystal engineering and it represents a higher stage of evolution of the subject.[3] Third generation crystal engineering deals with the design of functional solids in which the property and the structure are considered simultaneously,[4,5] and wherein the property is not taken as necessarily and inherently arising out of the structure.[3] It has been shown previously that the structure–property space may be divided into four quadrants in which the same or different crystal structures lead to the same or different crystal properties.[3] Materials with the same structure may have different properties and materials with different structures may have the same property. The former situation is known for the electronic properties where small changes within similar structures are amplified into larger differences in the property while the latter is observed, in say, the homology of differently structured proteins.[6] These types of lesser-known relationships between the structure and the property, at least lesser-known in the crystal engineering context, are now becoming more popular.[3–5,7]

Reports on third generation crystal engineering have just started appearing, and have been limited, to date, to examples of the design of the mechanical properties.[3–5,7] Flexible molecular crystals have potential applications in different fields, such as pharmaceuticals,[8] organic electronics,[9] optical devices,[10] molecular machinery,[11] artificial mechanosensors,[12] muscle-mimetic biomaterials,[13] and smart nanomaterials.[14] There are two major categories of such flexible crystals: irreversibly deformable plastic crystals[15] and reversibly deformable elastic crystals.[4] In the common type of plastic crystals, deformation takes the form of bending, which is possible along a particular direction because of its inherent structural anisotropy.[15] This restricts the overall utility of these crystals which cannot be used, for say, a purpose such as hand twisting.[7] Twisted helical crystals are useful in many diverse scientific areas, such as optical, electric or catalytic properties, enantiosensitive plasmonic sensors, negative-refractive index invisible metamaterials and their application in lithographic techniques.[16] The idea of obtaining such unusual crystal forms contrasts with the general brittleness associated with organic molecular crystals. Therefore specific crystal engineering techniques are needed.

In a recent result on elastic bending based on equivalence of σ-hole and π-hole interactions, we showed that one may profitably come outside of the traditional structure–property paradigm.[3] The typical σ-hole interaction that we had considered is halogen bonding, while the typical π-hole interaction is of the orthogonal electrostatic type that is without halogen atoms. In another recent result, we showed that halogen bonding is required in the design of hand-twisted helical crystals based on two-dimensional (2D) plastic deformation.[7] In the present communication, we show how these two ideas—halogen/hydrogen bond equivalence and orthogonality design—may be combined, within the concept of third generation crystal engineering, to target hand-twisted helical crystals based solely on hydrogen bonding, in other words without using halogen bonds.

Crystal synthesis, like all other syntheses, has seemingly independent strategic and methodological components.[2] A main strategy of crystal engineering is based on retrosynthesis using

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supramolecular synthons.[2] The methodology is the use of various interactions of different strengths, directionalities and distance dependence properties, in an optimal manner. To broaden the base of any strategy, one needs many different methodologies. The methodologies based on hydrogen bonding are still far more useful and general compared to those based on halogen bonding. That is why we attempted here to obtain hand twisted crystals based solely on hydrogen bonding, but noting however this halogen bonding seemed to be important in achieving the abovementioned properties. Additionally, the use of hydrogen bonds in crystal engineering always needs to be done judiciously because the selected donors and acceptors may also hydrogen bond to other groups in the molecule (unlike in halogen bonding).[17]

The starting point in the present exercise is the previously reported crystal structure of 4-chlorophenyl 4-nitrobenzoate (or 4-bromophenyl), **1**, which is 2D plastic and exhibits catemeric halogen bonds (Fig. 1a).[7] This halogen bond pattern is chosen for replacement with hydrogen bonds. The catemer O–H···O hydrogen bonded synthon common to phenols is suited for such a role (Fig. 1b).[18] Accordingly, the halogen free analogue, 4-hydroxyphenyl 4-nitrobenzoate (**2**) (Fig. 1b), was prepared and its crystal structure determined ($P2_12_12_1$, $Z = 4$; S1, ESI†). However, a problem now arose. The O–H group of the phenol is found to be coplanar within the ring plane owing to the resonance and the desired O–H···O catemer cannot be obtained for steric reasons. Stated in another way, the O–H hydrogen atom must be practically perpendicular to the ring if the desired halogen bond/hydrogen bond equivalence is to be secured. In the event, the crystal structure of **2** is completely different with other O–H···O (1.92 Å) and C–H···π (3.08 Å) interactions present (Fig. 1c). It is hardly surprising that such a crystal is brittle (S5, ESI†). A CSD study of torsional angle distributions in phenols, in which the 2- and 6-positions are unsubstituted, shows a predominance of low angles (0–20°; S6, ESI†). The conclusion is that the extended conjugation leading to OH and ring coplanarity must be suppressed if the OH group is to be oriented out of the molecular plane.

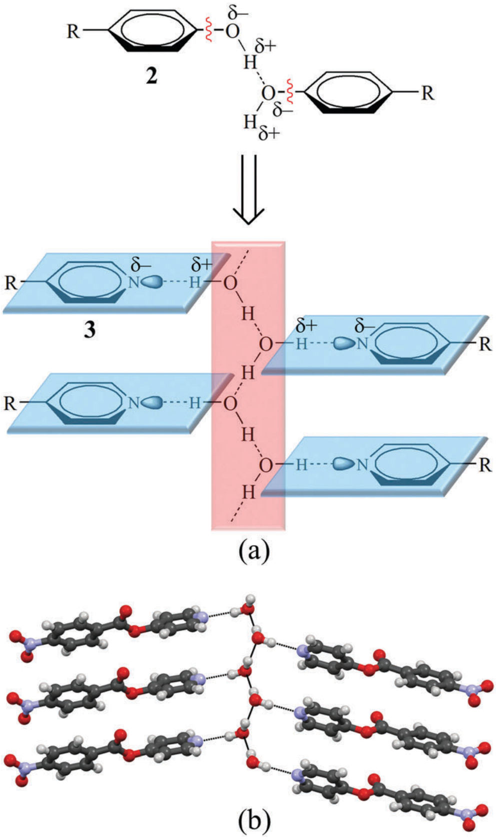

Fig. 2 (a) Molecular/supramolecular equivalence strategy driving the hydrogen bonded synthon (red) out of the ring planes (blue) in the title compound. (b) Crystal structure of $\mathbf{3}\cdot\mathbf{H_2O}$. Note that the desired structure has been achieved. R = 4-nitrobenzoate.

The retrosynthesis takes the form of finding a supramolecular equivalent[19] of the C–O covalent bond in the phenol—a link through which the resonance between the ring and the desired hydrogen bonded catemer synthon is removed. We searched for surrogates wherein (equivalents of) the C and O atoms would not be covalently bonded (Fig. 2a). Accordingly, compound **3** and water were identified. The pyridine N-atom is the equivalent of the C-atom in **2** while the N···H hydrogen bond from water to pyridine N is the supramolecular equivalent of the C–O covalent bond in **2**. The other H-atom from water participates in the formation of the desired O–H···O catemer.

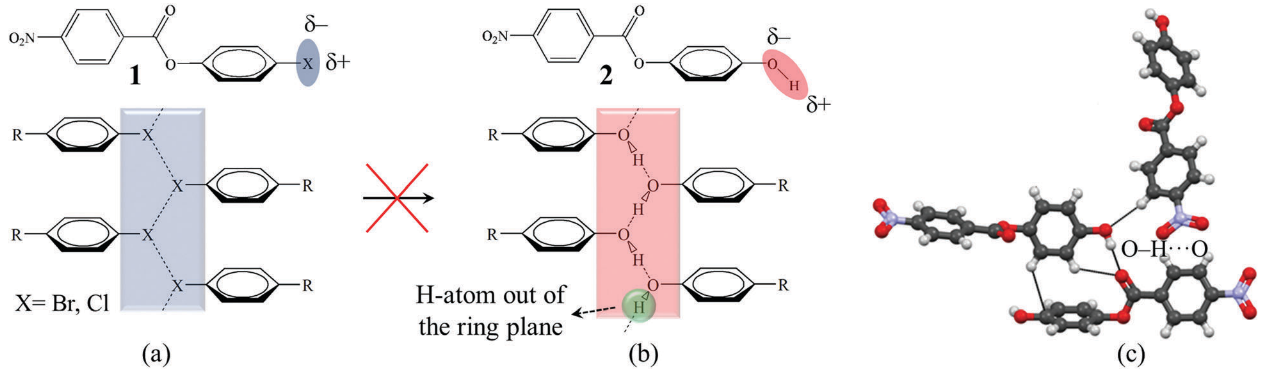

Fig. 1 (a) Halogen bonded 2D plastic crystal **1** from ref. 7. (b) If the O–H group is perpendicular to the phenyl ring in the targeted compound **2**, a similar crystal structure may be expected. (c) The observed crystal structure of **2**. Note that the O–H group is in the plane of the phenyl ring. Note also the absence of any hydrogen bonded catemer. The OH group is hydrogen bonded to ester carbonyl oxygen. R = 4-nitrobenzoate.

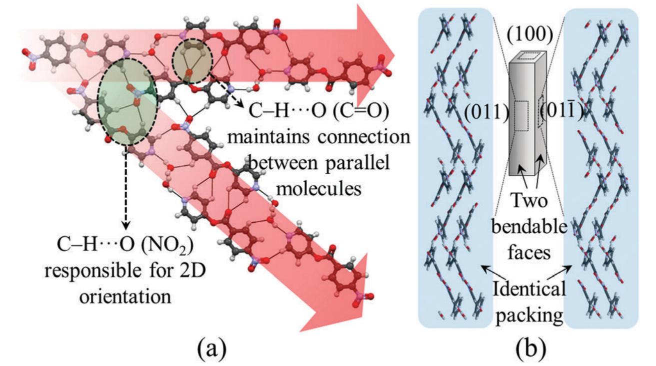

Fig. 3 (a) NO_2 group facilitating the 2D orientation of molecules through C–H···O interactions in the "rest of the structure". (b) Identical packing viewed down the equivalent major faces (011) and (01$\bar{1}$).

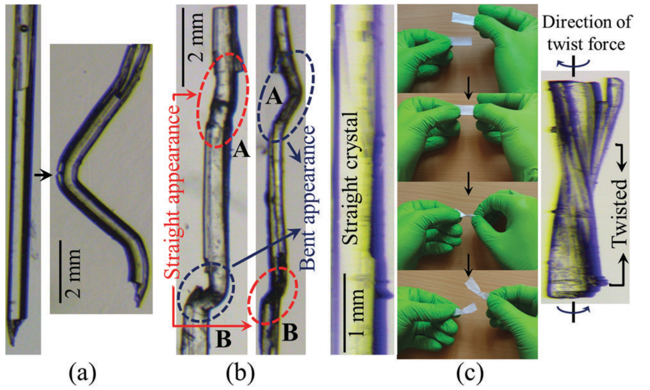

Fig. 4 (a) Plastic deformation in a crystal of **3·H$_2$O**. (b) A crystal bent along two different directions; therefore, only one bent site (**A** or **B**) is visible in any particular orientation and the other appears to be nearly straight. (c) Butter paper template twisting of a straight crystal.

Compound **3**, 4-pyridinyl 4-nitrobenzoate, was found to form the expected hydrate (S1, ESI†) and crystallizes in the $P2_12_12_1$ space group with $Z = 4$. Pyridine and phenyl rings are twisted about the ester linker at an angle of ~42°. The molecules are stacked (3.44 Å) along the [100] direction. The N-atom of pyridine is involved in O–H···N (1.98 Å) hydrogen bonds with water molecules and the other H-atom forms water chains (1.78 Å) (Fig. 2b). These interactions form parallel layers of supramolecular synthons which exactly follow the desired pattern. The NO_2 group again proves itself to be a dependable entity to maintain the necessary 2D molecular orientation in the rest of the crystal structure through C–H···O (2.51 Å) contacts (Fig. 3).[7] These auxiliary arrangements are very similar to those seen in compound **1** and accordingly the packing viewed down the major faces, (011) and (01$\bar{1}$), is identical. The fact that the "rest of the structure" is effectively insulated from the catemer synthons in both **1** and **3·H$_2$O** is key to the molecular/supramolecular equivalence design strategy. To summarise, the structure of **3·H$_2$O** is isomorphous to that of **1**. The relevant unit cell parameters are **1**: $a = 3.8$ Å, $b = 11.7$ Å, and $c = 27.12$ Å; **3·H$_2$O**: $a = 3.75$ Å, $b = 12.14$ Å, and $c = 26.33$ Å.

The pyridine–water interaction is frequently seen in the literature (1493 CSD hits) and a recent study discusses the propensity of the formation of hydrates in N-heterocyclic aromatic compounds[20] which have hydrogen bond acceptors but a paucity of donors. Such compounds have a high tendency towards the formation of hydrates[21] with the appearance of chains of water molecules. It is mentioned that such water chains also facilitate π···π stacking of the heterocyclic aromatic rings, and this is a key structural feature to obtain flexible crystals. The formation of hydrates depends on the accepting ability of the hydrogen bond of the heterocyclic N-atom; the greater the electron density on nitrogen, the higher would be the chance of hydration. In this respect, the presently considered system 4-hydroxypyridine, **3**, is a good hydrogen bonding functionality (ESP: −193 kJ mol^{-1}, S8, ESI†) for the formation of hydrates.

Long crystals of **3·H$_2$O** were sorted out to check their mechanical properties. When a straight crystal supported using a pair of forceps was poked at the middle, it created a permanent semi-circular arc shaped formation (Fig. 4a). This is a case of irreversible plastic deformation without a slip plane. It is unusual in that the phenomenon is being observed for the first time with strong hydrogen bonds (N–H···O and O–H···O) rather than halogen bonds, perpendicular to the bendable faces. The calculation of intermolecular interaction energies of significant synthons for model systems, using the counterpoise (CP) correction incorporated MP2/6-311++G(d,p) method, shows values of 18.38, 12.33 and 3.27 kJ mol^{-1} for O–H···N, O–H···O and C–H···O, respectively (S7, S9, ESI†). The C–H···O bonds are too weak to exert any significant effect[7] and the mechanical properties depend mostly on O–H···N and O–H···O interactions. A comparison with the earlier 2D halogen based systems in **1** and its bromo analogue shows that there is a reasonable correspondence between the X···X···X catemer in **1** and the O–H···O–H···O–H catemer in **3·H$_2$O** (Fig. 5). In a crystal engineering sense, these are the same structures after molecular/supramolecular exchange[19] and very similar mechanical properties are seen in both cases.

A straight crystal was also successively bent from two different major faces (Fig. 4b). This confirms and is the first demonstration of the existence of multiple plastic deformation directions in a purely hydrogen bonded system (Fig. 3b). Finally, crystals of **3·H$_2$O** were tested for the twisting experiment as previously described (Fig. 4c).[7] After the removal of the torque, the crystal was examined under a microscope and this confirmed the permanent twist shape of the initially straight crystal. The presence of multiple directions of bending is expected to help during the twist deformation by the simultaneous movement of molecules along different directions which is a primary requirement for helical deformation.

In summary, the present work is an example of third generation crystal engineering where a specialized halogen bonded system is converted into a generalized hydrogen bonded system to obtain soft twistable crystals. The target structure of **1** was sought to be replaced with a hydrogen bonded analogue. However, the selected compound **2** does not have the molecular attributes required for the preferred synthon orientations. Accordingly the C–X fragment in **1** is replaced by the N···H–O–H entity in **3·H$_2$O** and the desired structure was obtained showing the requisite

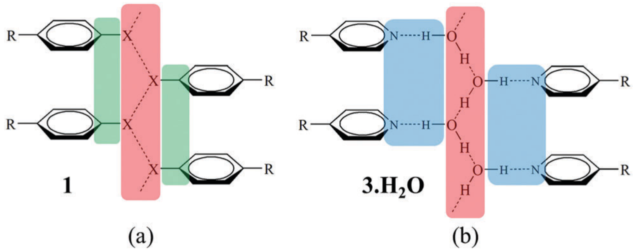

Fig. 5 Isomorphous halogen and hydrogen bonded crystals **1** and **3**·H_2O. The green molecular domains in **1** are replaced by the blue supramolecular domains in **3**·H_2O. R = 4-nitrobenzoate.

mechanical properties of hand-twistable plasticity. Such manipulations underscore the importance of molecular/supramolecular equivalence as a means of achieving halogen bond/hydrogen bond equivalence in higher generation crystal engineering.

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