

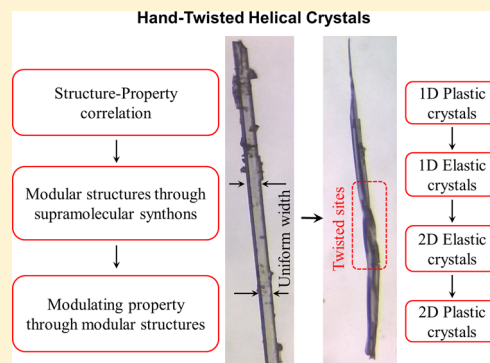
Crystal Engineering of Hand-Twisted Helical Crystals

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S Supporting Information

ABSTRACT: A strategy is outlined for the design of hand-twisted helical crystals. The starting point in the exercise is the one-dimensional (1D) plastic crystal, 1,4-dibromobenzene, which is then changed to a 1D elastic crystal, exemplified by 4-bromophenyl 4'-chlorobenzoate, by introduction of a molecular synthon –O–CO– in lieu of the supramolecular synthon Br...Br in the precursor. The 1D elastic crystals are next modified to two-dimensional (2D) elastic crystals, of the type 4-bromophenyl 4'-nitrobenzoate where the halogen bonding and C–H...O hydrogen bonding are well-matched. Finally, varying the interaction strengths in these 2D elastic crystals gives plastic crystals with two pairs of bendable faces but without slip planes. Typical examples are 4-chlorophenyl and 4-bromophenyl 4'-nitrobenzoate. This type of 2D plasticity represents a new type of bendable crystals in which plastic behavior is seen with a fair degree of isotropic character in the crystal packing. The presence of two sets of bendable faces, generally orthogonal to each other, allows for the possibility of hand-twisting of the crystals to give grossly helical morphologies. Accordingly, we propose the name hand-twisted helical crystals for these substances.



INTRODUCTION

Crystal engineering of organic molecular solids¹ has been practiced for the last 50 years or so. Initially, it was recognized that there is a connection between crystal structure and crystal property; this is exemplified by the work of Schmidt,² Wegner,³ Thomas,⁴ and others. Solid-state physical and chemical properties were explained on the basis of intermolecular interaction guided molecular arrangements in the crystals. The term “crystal engineering” was invoked by Schmidt² more as a challenge and in terms of setting long-term goals (Figure 1).

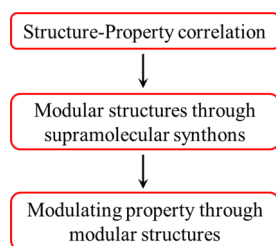


Figure 1. Development of crystal engineering.

This period also saw development of various models for crystal structure, notably by Kitaigorodskii,⁵ Desiraju,⁶ and Etter,⁷ to explain observed crystal structures in terms of the packing features and/or the intermolecular interactions involved. The emphasis next shifted to actual strategies and logic-driven methodologies of crystal design: The concept of the supramolecular synthon was identified as being crucial to the planning of crystal synthesis.^{8,9} This phase of the subject continues until today with the strong modular capability of the

synthon being applied in both structural chemistry^{10–16} and biology,^{17–20} but the general emphasis was on structure rather than property design. In the present work we have tried to take a step in this latter direction and to alter properties, even drastically, within a particular structure type. In this sense, the strict structure–property correspondence seen in earlier times need not necessarily always be observed. We suggest that one may now design a desired solid-state property starting with a crystal that does not have it, rather than optimize a property in a crystal that has been obtained through an initial serendipitous result. There is a subtle shift in emphasis in that the design strategy is developed heuristically, but of course with structural inputs. Taking up the design of soft flexible crystals,^{31,33} this work is concerned with plastic and elastic crystals.

The original 1989 definition of crystal engineering⁶ foresees the development of the subject as (a) understanding of intermolecular interactions in the context of crystal packing; (b) design of new solids where design pertains to structure only; and (c) obtaining desired physical and chemical properties as described in the present paper. These stages naturally telescope chronologically.

Crystal property design is an attractive and rapidly growing area of organic crystal engineering today. Mention should be made of work on thermo- and photosalt materials,^{21–24} colored crystals,²⁵ semiconductor crystalline materials,^{26,27} self-healing crystals,²⁸ mechanically deformable crystals,^{29–34} pharmaceutical compounds,^{35,63} and others.^{36,64} Flexible solids, which include irreversibly bendable plastic and reversibly

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bendable elastic crystals, are of core interest because of applications to many fields such as optical devices,^{37,38} organic electronics,^{39,40} artificial mechanosensors,⁴¹ molecular machinery,⁴² muscle-mimetic biomaterials,⁴³ smart nanomaterials,⁴⁴ and pharmaceuticals.^{45–47} In general, one-dimensional (1D) plasticity with a single pair of opposite bendable faces results from slip-plane-assisted structural anisotropy,²⁹ whereas isotropic interlocked packing gives elasticity.³² These studies and others show the different structural and interaction requirements for plastic and elastic deformation and bending of molecular solids.

Naturally occurring helical or twisted crystals have been known for a few centuries.⁴⁸ These twisted architectures are sought out today as functional materials targeting specific optical, electric, or catalytic properties, negative-index metamaterials or invisible materials, and enantiosensitive plasmonic sensors.⁴⁹ Recent developments in lithography techniques and metamaterials have stimulated new interest in older studies on chiroptic materials.⁵⁰ These materials are characterized by different absorptions of circularly polarized light which makes for different refraction. Helical crystals are generally formed through different methods of crystallization such as slow evaporation of solvent, sublimation, or diffusion-limited growth in different types of gel matrix.⁴⁹ All these techniques are highly uncertain and hardly predictable to obtain helical crystal for any given unknown system. In this scenario, a predictable and easy technique for crystal growth would be useful. Nevertheless, no strategy has been adopted so far to manually fabricate twisted crystals. Crystal engineering principles are relevant here because they begin with a bottom-up approach from intermolecular interactions. Twisted crystals represent changes in the bending direction in a periodic way. This suggests the requirement of multiple deformation directions in the crystals to make them helical or twisted.

RESULTS AND DISCUSSION

In this paper, we report a number of crystals with multiple sets of plastically bendable faces, which we then show are twistable. In general, the incorporation of plasticity and multiple bendable faces within the same crystal would appear to be contradictory²⁹ in terms of the respective structural requirements. Multiple bendable faces would imply more crystal isotropy, and this opposes the requirements of plastic bending which requires interaction anisotropy. The incorporation of various mechanical properties is achieved in a stepwise and gradual manner (Figure 2).

The initial step starts with a common 1D plastic crystal with clear-cut interaction anisotropy. In the next step, this is changed to elastic by varying molecular orientation so that more isotropic, interlocked packing is favored.³² The 1D elastic crystals are next modified to two-dimensional (2D) elastic through further structural changes.^{51–53} Finally, the interaction strengths^{54,55} in the 2D elastic crystal are changed using known chemical principles so that the isotropy is decreased to the extent that plasticity ensues. However, because the basic structural topology is not changed, there are no slip planes in these 2D plastic bendable crystals. Most of these modular crystal structures are sustained through halogen bonds,^{56,57} which are of critical importance in the entire design exercise. The presence of more than one pair of bendable faces makes these compounds more effective toward deformation. This last class with 2D plasticity represents a new type of plastically bendable crystals. The application of hand-applied twisting

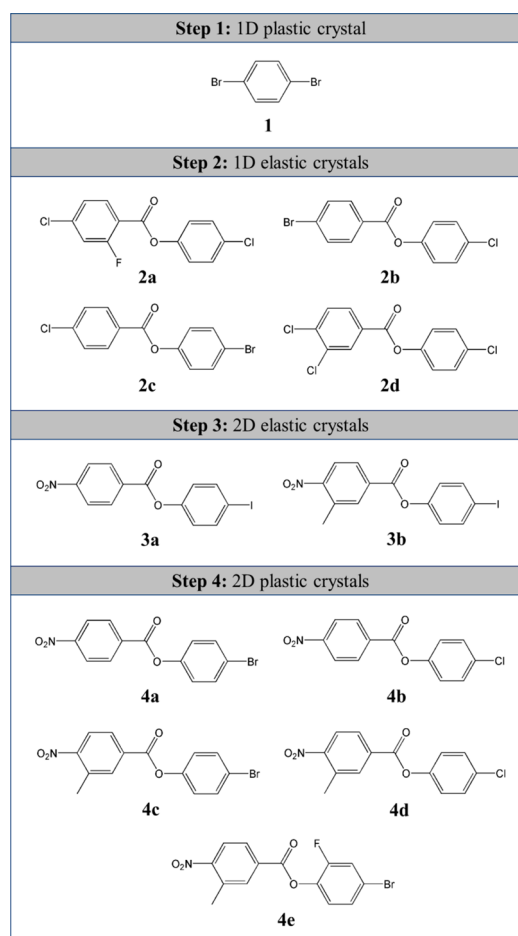


Figure 2. Flow chart of design steps in the present work.

along the lengths of the 2D plastic crystals produces permanent twisting. Application of the same manual procedure (hand twisting) on common 1D plastic crystals failed to achieve the same result. In a topological context, we present here the design of hand-twisted helical crystals of achiral molecules without the use of external chiral additives.

We now describe the four steps of the property design.

Step 1: Selection of 1D Plastic Crystal: 1,4-Dibromobenzene, 1, and Strategies toward Elasticity in Step 2. 1,4-Dibromobenzene (**1**) crystallizes in the $P2_1/n$ space group ($Z' = 0.5$). The phenyl rings are stacked (3.53 Å) along the needle direction [101] (Figure 3a). These stacked columns are extended along the [010] direction with Br...Br (3.77 Å, $\theta_1 = 93.9^\circ$, $\theta_2 = 165.7^\circ$) type-II halogen bonds, constructing slip planes. There are also C–H...Br (d : 3.24 Å) dimer synthons along the same direction. The third direction [001] also consists of C–H...Br (3.14 Å) hydrogen bonds. A rodlike crystal supported from (001) plane was poked on the opposite face, resulting in permanent distortion (Figure 3c) or plastic bending, but it was brittle from the other faces and also toward external twisting force (see Figure S12). This results in 1D plastic bending only. This is a common compound, and 1D plasticity is also common enough a phenomenon now. However, this is the first report of 1D plastic deformation in this compound.

Design of an Elastic Bendable Crystal from a Plastic Crystal. The next step involves upgrading **1** to an elastic crystal. In other words, how does one incorporate more isotropic

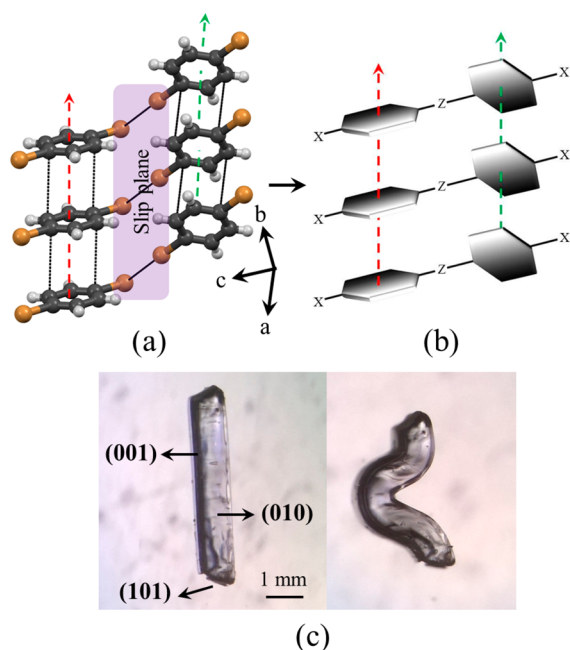


Figure 3. (a) $\pi\cdots\pi$ and Br \cdots Br type-II contacts in the crystal structure of **1** with a slip plane (lilac). (b) Br \cdots Br synthons are replaced by molecular synthons (Z) in Step 2 so that the rings can be oriented along different directions (red and green arrows) in the model system. (c) Plastic deformation of a crystal of **1** on (001) face.

character in the packing? For this, we considered some molecular modifications. In **1**, weak halogen bonded adjacent stacked columns face along different directions (Figure 3a, red and green dashed arrows, $\sim 57^\circ$). The breaking of these weak halogen bonds between differently oriented adjacent columns is expected to lead to permanent molecular movement or plastic deformation. In order to restrict the breakage, alternate Br \cdots Br supramolecular synthons were replaced with molecular synthons, namely, linker Z (Figure 3b). Covalent linking of two Ph-rings along the molecular axis prevents independent migration of columns.³² To increase isotropic packing, the $-\text{Ar}-\text{Z}-\text{Ar}-$ compound selected should be nonplanar and furthermore should be easy to make. A Schiff base (Z is $-\text{CH}=\text{N}-$) linker proved to be reasonable in this regard,³²

but suffers due to moisture sensitivity. As an alternative, the amide linker $-\text{NHCO}-$ similar to the imine group with respect to size and shape, was selected.

Choosing the Molecular Linker: Cambridge Structural Database Study. The question, however, is whether or not the amide linker can consistently maintain the phenyl rings in a nonplanar orientation. Compounds **P1** and **P2** (see Figure S13) were prepared for this. The crystals of amide molecules produced undesired plasticity instead of elasticity. We tried to obtain the crystal structures of the amides many times, but poor internal crystal quality restricted us in so doing. The failure of the model initiated us to use the Cambridge Structural Database (CSD) to ascertain the behavior of amides in this context. The CSD was searched for simple amides, Ph-NHCO-Ph, wherein the 2,6 positions on the two phenyl rings are substituted only with H atoms; 461 hits were obtained. The histogram (Figure 4a) shows a preferential orientation for torsion angles in the range $40\text{--}80^\circ$ (202 molecules, 43%) which is useful for our purpose, but there are also hits with angles in the range $0\text{--}20^\circ$ (172 molecules, 37%) which is not so desirable. Therefore, we felt that the amide linker is not completely reliable to achieve a nonplanar molecular structure, and perhaps the $-\text{NHCO}-$ fragment allows sufficient conjugation between the two phenyl rings. An isoelectronic fragment, say an O atom with less electron donating ability, could lower the tendency toward conjugation and with it a planar structure, so we selected phenol esters where the linker Z is $-\text{OCO}-$. The CSD analysis for these compounds (Figure 4b) shows a strong preference for inter-ring torsion angles between 40 and 90° (379 out of 415, 91%), showing that the ester group $-\text{OCO}-$ is more suitable than the amide $-\text{NHCO}-$ as a linker for nonplanarity.

Step 2: 1D Elastic Bendable Crystals. Considering the ester group as a linker, we prepared compounds **2a–2d**. 4-Chlorophenyl 4-bromobenzoate (**2b**) has two polymorphs, forms I and II. Both crystallize in the $P2_1/c$ space group ($Z' = 1$) with phenyl–phenyl torsion angles of 48 and 57° respectively (Figure 5a). In form I, molecules are $\pi\cdots\pi$ stacked (3.45 \AA) along the b -axis. The Br-atoms form type-II Br \cdots Br (3.59 \AA , $\theta_1 = 127.0^\circ$, $\theta_2 = 165.1^\circ$) contacts, and the Cl-atoms form type-I Cl \cdots Cl (3.63 \AA , $\theta_1 = \theta_2 = 157.8^\circ$) contacts (Figure 5b). The halogen bonded synthons continue along [001] to

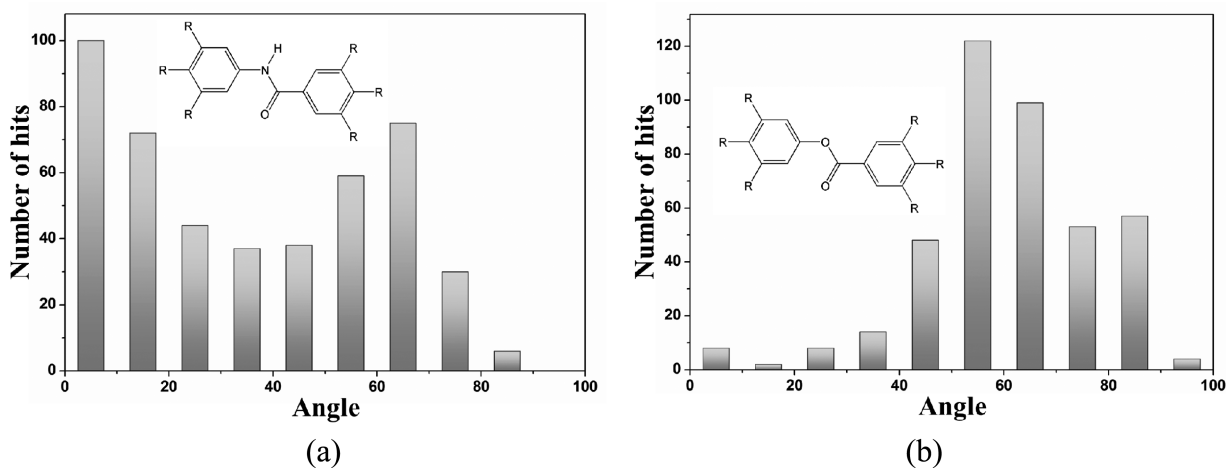


Figure 4. CSD (November 2014, including updates until May 2015) studies of: (a) amides, PhNHCOPh, and (b) esters, PhOCOPh to show inter-ring angles.

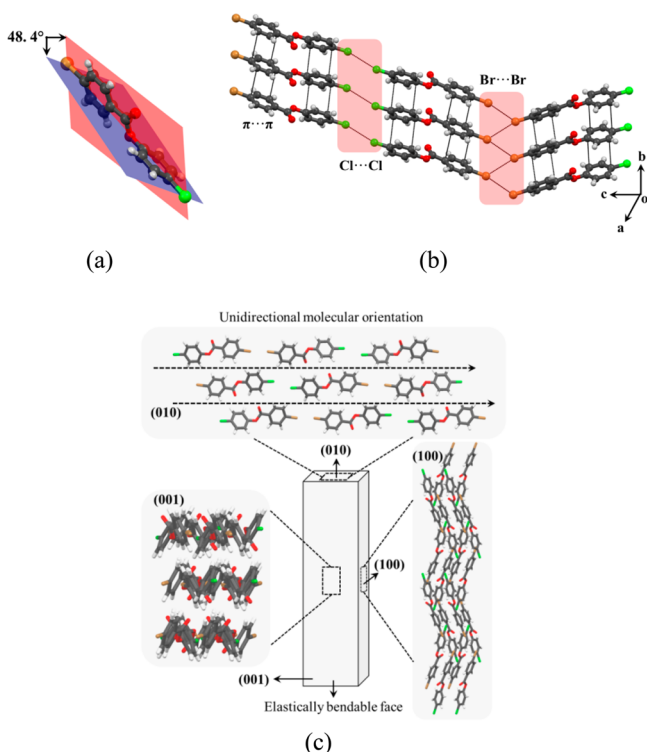


Figure 5. Crystal packing and representative synthons in form I of **2b**: (a) Torsion of phenyl rings at an angle of $\sim 48^\circ$. (b) Halogen bonds between π -stacked columns involving Br (type-II) and Cl (type-I) continue along [001]. (c) Schematic presentation of crystal morphology with marked faces. Molecules show unidimensional packing along [001].

form parallel tapes, forming the 1D packing (Figure 5c) in the ac -plane. These parallel tapes are connected via C–H \cdots O (2.56 Å) and C–H \cdots Cl (3.2 Å) hydrogen bonds. The comparable energy of interactions along orthogonal directions makes this crystal structure isotropic. Form II also has an isotropic structure with type-II (3.86 Å, 82.7° , 148.3°) and type-I (3.9 Å, 142.3°) Br \cdots Br synthons (Figure 6), but the presence of C–

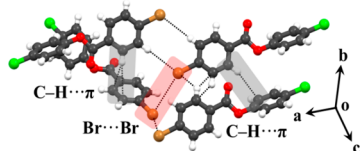


Figure 6. Representative supramolecular synthons in form II of ester **2b**.

H \cdots π (2.84 Å, 3.05 Å, 3.03 Å) interactions removes the layering of $\pi \cdots \pi$ stacked molecules. **2c** and **2d** are isostructural to the form I of **2b** (see Figures S5 and S7). The packing of **2a** (Figures S5–S7) is also very similar to that of type-II halogen bonds on both sides. There are also some other compounds (see compound **B1** in Figure S14) which do not follow the model and are not discussed further. Form-II of **2b** is of this type. Thus, while the strategy works, it is not 100% efficient, but it is good enough to make further progress.

Mechanism of Elastic Bending. Crystals of compounds **2a–2d**, including polymorphs, were tested for bending. About 5 mm long, thin, straight crystals of **2a**, **2b** (form I), **2c**, and **2d** were supported from the major face [(100) for **2a** and (001)

for others] and then poked on the opposite face, resulting in a bent morphology which was restored to the initial state after removal of force, i.e., elastic crystals (Figure 7a) (also see Video

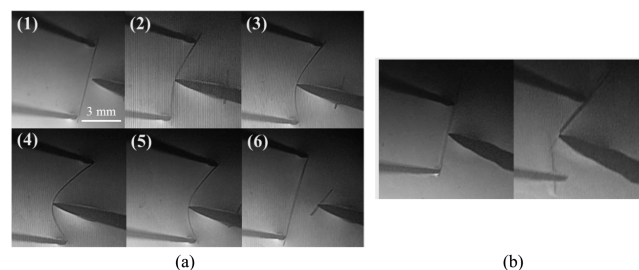


Figure 7. (a) Bending of a 1D elastic crystal of **2b** (form I) from the (001) face (panels 1–6). This operation may be performed repeatedly without crystal breakage. (b) Attempt to bend the same crystal from the other face parallel to the needle axis broke the crystal immediately.

S1). The experiment may be repeated. When these crystals were poked on the other faces along the needle axis, they broke (Figure 7b) (see the last part of Video S1 of **2b** form I). These crystals can only be bent from one face, and hence are 1D elastic. The form II of **2b**, without $\pi \cdots \pi$ stacking, was found to be brittle toward external mechanical stress (Figure S10), suggesting the importance of $\pi \cdots \pi$ stacking for elasticity.

A possible mechanism for elastic bending is illustrated in Figure 8. The direction of the halogen bonds are perpendicular to the bending face and are at equilibrium in the pristine crystal. During bending (Figure 8b), the $\pi \cdots \pi$ stacking acts as a spring, permitting regular structural changes at the bent site where all the halogen bond distances and angles may not be consistent. At the inner side, the packing is little compressed which may result in shorter halogen bond distances and angles. There is a concomitant expansion at the outer side causing slightly longer halogen bond distances and larger angles. The middle portion remains largely unaffected. The polarizable nature of halogen bonding allows for these deformations. These structural deformations during bending destabilize the system with respect to the initial thermodynamic equilibrium state and generate mechanical strain at the site of bending. At this stage, electrostatic type-II halogen bonds, which operate at longer distances, can bring the whole system back to its initial thermodynamic position, relieving the bent crystal from the stress. This is why the bending phenomenon is elastic.

Step 3: Design of Two-Dimensional Elastic Bendable Crystals. Strategy to Make 2D Elastic Bendable Crystals. Access to more than one major bendable direction (here, two) requires nearly mutual perpendicular orientations of the molecules (Figure 9), in other words, a herringbone arrangement (Figure 9b). The literature shows that orthogonal C–H \cdots O interactions are potential contacts to maintain such an arrangement.^{51–53} Compound **E3** however is seen to display only 1D elasticity, and there are no side-to-end orthogonal C–H \cdots O interactions (see Figure S15). Then, we used the NO₂ derivative and prepared 4-iodophenyl 4-nitrobenzoate (**3a**) and 4-iodophenyl 3-methyl-4-nitrobenzoate (**3b**) (Figure 2). These crystals showed the desired 2D pattern, suppressing the problematic issues. The structures are explained hereafter.

Compound **3a** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z' = 1$ and the phenyl–phenyl torsion angle 53° . Molecules are $\pi \cdots \pi$ stacked (3.45 Å) along the a -axis. The type-II I \cdots I (3.82 Å, 130.5° , 165.1°) halogen bonds (Figure 10)

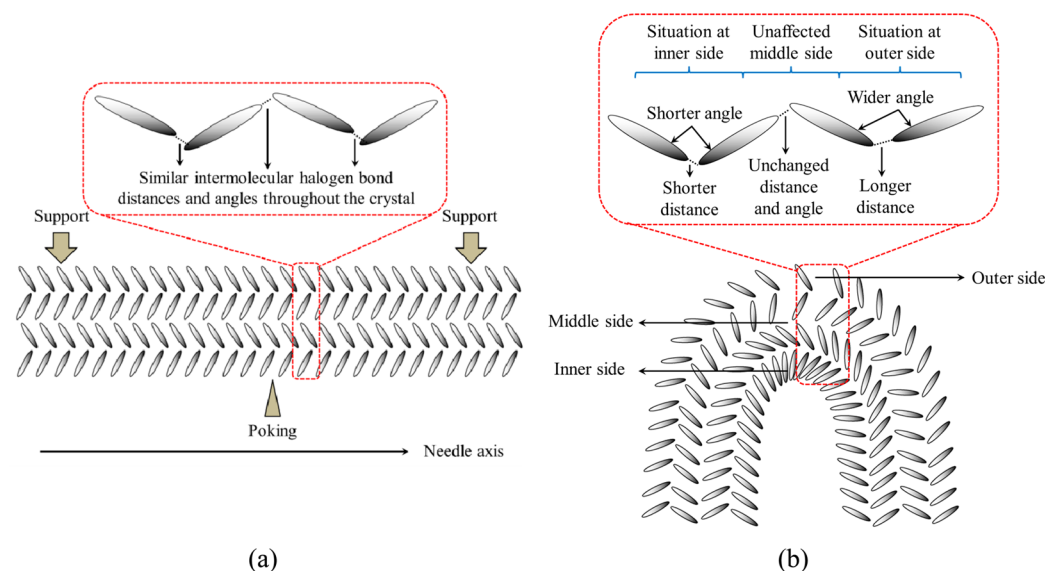


Figure 8. Schematic representation of the bending mechanism, (a) before bending and (b) during bending.

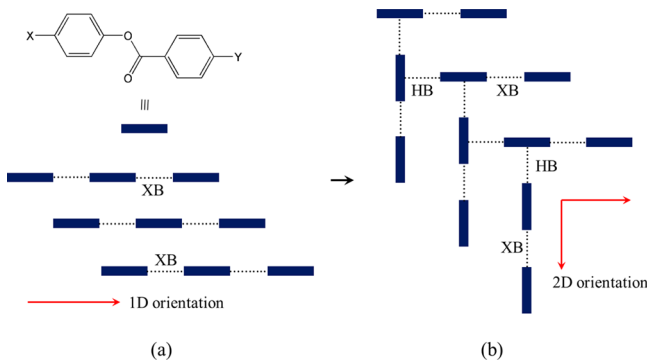


Figure 9. Schematic illustration of (a) parallel halogen bonded (XB) tapes present in 1D elastic crystals ($X = Y = \text{halogen}$) in this study and (b) design strategy for 2D elastic crystals through $\text{C-H}\cdots\text{O}$ ($X = \text{halogen}$, $Y = \text{nitro}$) hydrogen bonds (HBs).

connect the stacked columns. These halogen bonded units with NO_2 groups at the end form $\text{C-H}\cdots\text{O}$ (2.48 Å, 2.58 Å, 2.55 Å) synthons in a side-to-end fashion along $[011]$ and $[0\bar{1}\bar{1}]$ (Figure 10b), which eventually orient the molecules at an angle of $\sim 45^\circ$ besides keeping them parallel, like in the 1D cases discussed earlier. Such orientation makes the packing identical in both major faces (011) and (0 $\bar{1}\bar{1}$) (Figure 10c). The $\text{C-H}\cdots\text{O}$ (2.40 Å) synthons involving ester and $\text{C-H}\cdots\text{I}$ (3.36 Å) interactions hold the adjacent tapes. Compound **3b** is isostructural to **3a** (see Figures S5 and S7).

Long, thin crystals of both **3a** and **3b** were found to be elastic (see Video S2) when poked on any of the major faces, (011) or (0 $\bar{1}\bar{1}$). The availability of two bending directions makes the crystal 2D elastic. The mechanism of deformation is very similar to that of the 1D case. However, here one end of each molecule is involved in similar halogen bonds, whereas the other end has $\text{C-H}\cdots\text{O}$ hydrogen bonds. The system shows reversible bending supported with combined influence from halogen and hydrogen bonds.

Step 4: 2D Plastic Bendable Crystals. Methodology. Since halogen bonds play a role for elasticity in compound **3** and other previously reported cases, lowering their strength, vis-à-vis the $\text{C-H}\cdots\text{O}$ bonds with retention of the 2D

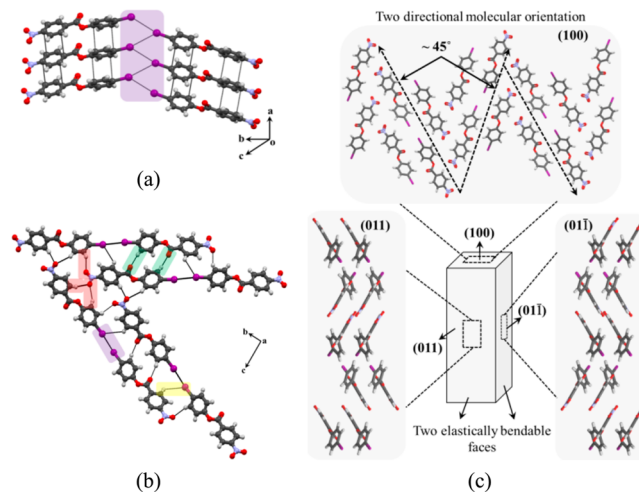


Figure 10. Crystal packing and some typical synthons in **3a**. (a) Type-II $\text{I}\cdots\text{I}$ halogen bonds (violet) exist along $[011]$ and $[0\bar{1}\bar{1}]$. (b) $\text{C-H}\cdots\text{O}$ (NO_2) (red) synthons are present along the same directions; other interactions like $\text{C-H}\cdots\text{O}$ (carbonyl) (green), $\text{C-H}\cdots\text{I}$ (yellow) are also highlighted. (c) Schematic shape of crystal is shown with labeled faces. $\text{C-H}\cdots\text{O}$ hydrogen bonds orient the molecules along two different directions, $[011]$ and $[0\bar{1}\bar{1}]$. The packing in both (011) and (0 $\bar{1}\bar{1}$) planes are similar.

geometry, could affect this particular property. It has been shown that varying halogen bond strength by replacing higher halogens with lower halogens can affect the mechanical property.⁵⁴ The change in mechanical property (plastic to elastic) by changing the halogen bond strength within isostructural systems is well-documented.⁵⁵ In this context, the strength of halogen bonds of the step 3 compounds was varied by substituting the I atom in **3** with Br and Cl, which are expected to form weaker halogen bonds (compounds **4a–4e**, Figure 2). For comparison, the approximate energies of a $\text{I}\cdots\text{I}$, $\text{Br}\cdots\text{Br}$ and $\text{Cl}\cdots\text{Cl}$ interaction are 10, 7, and 5 kJ/mol ⁵⁵ and are comparable with the $\text{C-H}\cdots\text{O}$ bonds in the structure.

Compounds **4a–4e** are isostructural to **3a** (Figures S5–S7). They also have $\text{C-H}\cdots\text{O}$ (NO_2) (2.50 Å, 2.61 Å, 2.52 Å) and

type-II halogen bond mediated 2D orientation (Figure 11) as seen previously in step 3.

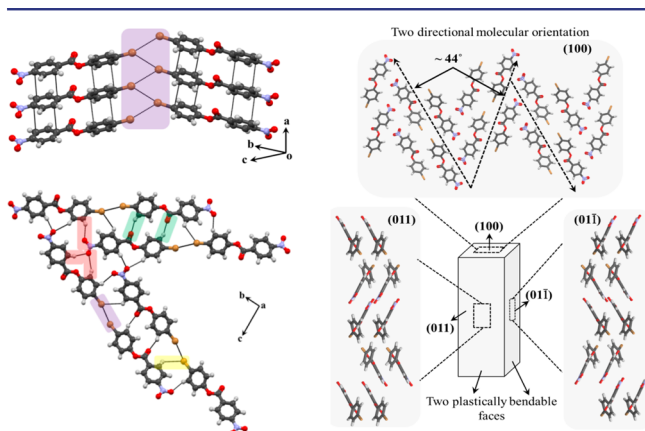


Figure 11. Packing in **4a** identical to that in **3a**. Type-II Br \cdots Br (lilac) and C–H \cdots O(NO₂) (pink) contacts persist along two directions, [011] and [011].

Plastic Bending. The bending property of crystals of each compound was tested in a similar manner. When a crystal of **4a** supported from the (011) face was poked on the opposite face, it took a curved shape (Figure 12) but did not regain the

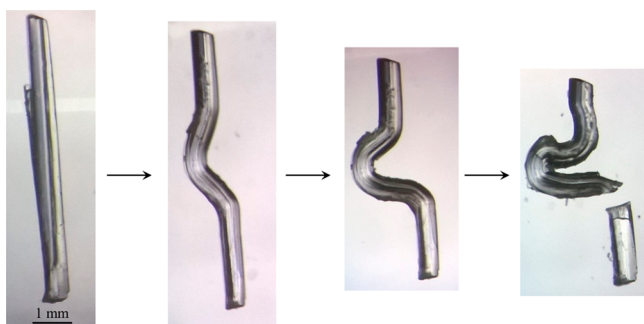


Figure 12. Images of progressive plastic bending in a crystal of **4a** on the application of external mechanical force.

original shape upon unloading of the deformation force. Hence, the bending is irreversible and thus plastic. All the other compounds in step 4 exhibit the same behavior.

2D Bending. To check the 2D plastic bending property, an undistorted crystal of **4c** was first bent (position 1) on either of the major faces along the needle axis (Figure 13). Thereafter, this bent crystal was further bent on the other face (position 2) along the needle axis. In the Figure 13a the two different directions of bending are difficult to visualize. The same crystal is then viewed from two different angles separately. In Figure 13b, bent position 2 parallel to the plane of paper is clearly visible, but position 1 is directed nearly perpendicular to the plane of the paper and appears nearly straight, and vice versa for Figure 13c. These clearly point to the presence of two different directions for plastic bending in nearly isotropic, interlocked crystals. This type of behavior deviates from earlier structure–property rationalizations which are based on the idea that isotropic packing leads to elastic behavior.

The replacement of relatively strong I \cdots I interactions by weaker Br \cdots Br or Cl \cdots Cl interactions means that the restoring capacity of the crystal (which is needed for elasticity) is reduced

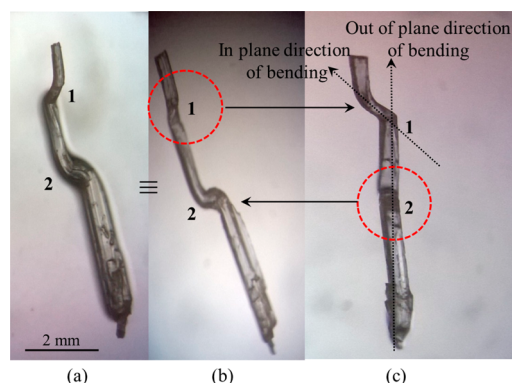


Figure 13. 2D plastic bending of **4c**. (a) A crystal bends at two positions (1 and 2) along two different directions. (b) and (c) The same crystal is oriented in such a way so that only one bending side is visible. The slanted arrow in (c) shows direction of one of the bending faces, and the other one represents the bending direction perpendicular to plane of the paper. The angle between two bend faces is $\sim 45^\circ$, which is similar to the crystallographically determined angle.

to the extent that permanent molecular movement is again seen. That is why step 3 compounds are elastic but isotropic (at the molecular level as well as at the crystallographic level) while step 4 compounds are plastic. This explanation raises a question as to why the same atoms (Br, Cl) with similar type-II geometries exhibit a different bending property, elastic and plastic, for step 2 and 4 compounds, respectively. In order to answer this question, we calculated the electrostatic potential (ESP) surface maps for Br in two model compounds, **5** and **6** (Figure 14). The higher ESP value for the Br (137 kJ/mol)

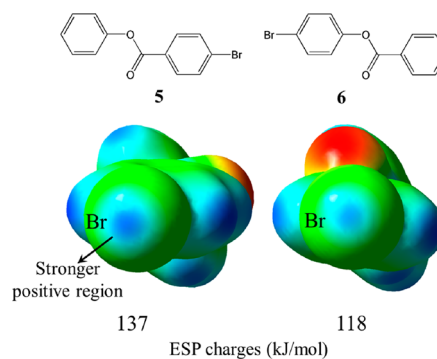


Figure 14. Electrostatic potential (ESP) maps for model systems **5** and **6**.

attached to the electron-withdrawing carbonyl aromatic ring, compared to that of the Br (118 kJ/mol) connected to electron-donating phenolic part suggests the presence of stronger halogen bonding ability in the former (**5**), that is, in the step 2 examples. Thus, the weaker nature of the type-II Br \cdots Br interactions result in plasticity in the step 4 compounds. Generally, our observations are in accord with the fact that the shear modulus of these crystals is on the order of 5 GPa (for a measured Young's modulus = 15 GPa),⁶⁵ and with a crystal size of $5 \times 0.2 \times 0.2 \text{ mm}^3$, it is expected that one needs around 0.15 J/mm^3 , in other words, $\sim 28 \text{ kJ/mol}$, to plastically deform the crystal (see Supporting Information for details). This is comparable with the energies of individual halogen and weak hydrogen bonds involved ($\sim 7 \text{ kJ/mol}$). The implication is that

these types of interactions could be quite useful in the design of similar elastic and plastic organic crystals.

Hand-Twisted Helical Crystals. The crystals of the step 4 compounds were examined and tested for hand-twisting. Initially, we faced many difficulties in performing the twisting experiment on straight crystals due to their small size. Then, a butter (waxy) paper based template method was applied to do the same. A straight crystal (Figure 15a) of **4b** was placed at the

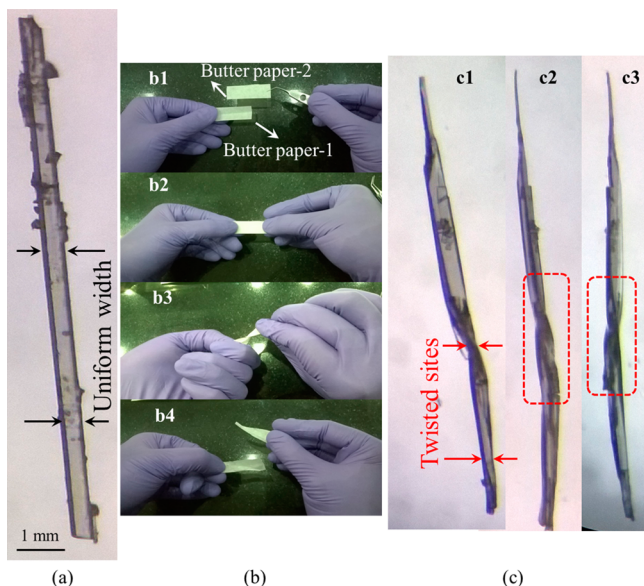


Figure 15. (a) Undistorted crystal of **4b** before performing the twist experiment. The same crystal on (b1) butter paper-1 and (b2) covered with another butter paper-2. (b3) Twisting of the butter paper encapsulated crystal by hand. (b4) After releasing the twist force. (c1–c3) Enlarged view of the hand-twisted helical crystal as seen from different angles. The twisting at the middle is marked with red dotted lines.

middle of a rectangular shape butter paper (Figure 15b1, butter paper-1) and covered with another similar size paper (Figure 15b2, butter paper-2). The two ends of the papers were then gently held. Then, the papers were twisted slowly across the plane of the paper (as in a toffee wrapper) to a torsion angle of $\sim 150^\circ$ (Figure 15b3). The twisting force was then retracted (Figure 15b4). The pair of butter papers acts both as holder and support during the process of hand-twisting of the soft crystal. The resulting crystal was examined under the microscope. The enlarged images in Figure 15c1–c3 show the presence of a twist in the crystal. The twist is clear at the middle and less clear at the bottom due to the fracture of the crystal. Other compounds of this series also show similar twisting. This whole process describes the manual crafting of twisted crystals which we accordingly term “hand-twisted helical crystals”. A similar experiment on the crystal of common 1D plastic 1,4-dibromobenzene (**1**) results in breakage of the crystal into pieces without any sign of twist (Figure S12).

Helical or twisted crystals are crystals wherein there is a bending in different directions in a grossly periodic way (Figure 16). The manual twisting can be explained as combination of multiple steps. First, any position of a crystal starts to bend along anyone of the two bending directions (arrow 1, coming out of the plane of the paper). At the same time, the adjacent positions begin to deform along the other direction (arrow 2 on the plane of the paper). Here, the bending along two different

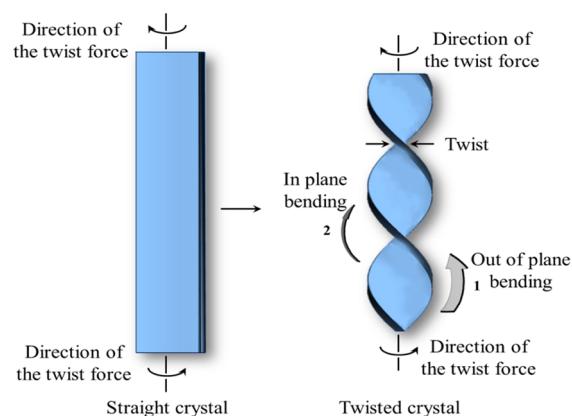


Figure 16. Schematic twisted crystal with opposite directions of bending creating a torque, shown as arrow-1 (out of the plane) and arrow-2 (in the plane bending), the simultaneous application of which generates a helical shape.

directions is possible because of the existence of two bending faces in the crystal. This process can continue periodically to form a complete helical shaped crystal.

CONCLUSIONS

We have shown here that preidentified properties in a molecular crystal, in this case plastic and elastic mechanical deformation, may be deliberately engineered with a controlled variation of intermolecular interactions. In the present example, a series of aromatic compounds including halogenated phenyl benzoates are a convenient template to illustrate these ideas. We started with a normal plastic crystal, namely, 1,4-dibromobenzene, and have in succeeding steps introduced 1D and then 2D elasticity, and finally, by halogen bond manipulations, 2D plastic deformation. The fact that a nominally isotropic packing can lead to plastic deformability is a new paradigm in the mechanical property engineering of molecular crystals. There is accordingly an evolution in the borderline region between elastic crystals and this new generation of plastic crystals. When does an isotropic packing lead to elasticity and when does it lead to 2D plasticity is an open question asked by this study. We also show that it is not really necessary to have a slip plane to induce plastic deformation in a molecular crystal. As far as helical shaped crystals are concerned, these have long since been known, and these morphologies are reported as occurring under certain conditions of crystal growth and solvent. The present work shows that one may apply a deliberate crystal design strategy that can be applied in a predictable way to obtain helical crystals to obtain the first hand-twisted helical crystals. Crystal engineering has been practiced for roughly 50 years, and it is now possible to discern certain historical trends from the early years. The early days of crystal engineering dealt with structure–property correlations based on intermolecular interactions. Next, there was a shift in emphasis toward synthon based logic-driven design of desired crystal structure with predictive ability. At the present time, and in the example provided in this paper, it is seen that both structure and property are modular attributes. Therefore, both can be subjected to design strategies, perhaps independently. Whether or not such exercises would constitute a new third generation of crystal engineering is something that can only be known if and when more examples are revealed.

There is still another aspect of this study that is of relevance especially when crystal engineering is taken as a form of supramolecular synthesis.⁸ It should be clear to the practitioner of synthesis that any synthetic plan such as one based on synthon based retrosynthesis is a general outline which provides a roadmap for actions, but it is only the experiments done in the laboratory that determine the actual route taken. In the end, these details are everything because they take the synthesis “through the region of uncertainty”.⁶⁶ The role of imagination and intuition cannot be denied in synthetic chemistry. Attempts to disguise the intuitive component in any synthetic exercise through some kind of thought readjustment and a repackaging of partial thoughts that preceded the successful synthetic step in a more causative idiom falsely allows one to imagine that the process of discovery arose entirely from intellectual thinking and a purely logic-driven reductionist thought process.⁶⁷ The steps described above for the design of a 2D plastic crystal are just that, a menu or a recipe for crystal engineering of such materials. The general strategy would work in many cases, but the success in carrying out the plan would depend on how one addresses details that emerge in the actual experiments. In the end, difficult syntheses are not only difficult to carry out but also difficult to communicate. The transition between reason and imagination,¹⁰ between science and art, is not at all new to organic synthesis.⁶⁸ It is our contention that this phase has surely arrived now in crystal engineering and that it will be contained only by the imagination of its practitioners.

EXPERIMENTAL SECTION

Synthesis and Crystallization. Synthesis and crystallization procedures of steps 2–4 compounds are given in Figure S1.

Single Crystal X-ray Diffraction. X-ray data of all crystals were collected on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromator Mo K α radiation, with an attached Rigaku low temperature gas spray cooling device. The data were processed with the Rigaku CrystalClear 2.0 software.⁵⁸ Structure solution and refinements were executed using SHELX97^{59,60} implemented in the WinGXsuite.⁶¹ All the non-hydrogen elements were refined anisotropically and hydrogen atoms were refined isotropically. Hydrogen atom positions were fixed based on riding model. The crystallographic data are given in the Figure S3. The face indexing images of the crystals are given in the Figure S4.

Powder X-ray Diffraction. Powder X-ray data (Figure S8) were collected on a Philips X'pert Pro X-ray powder diffractometer with attached X'cellerator detector. The sample was scanned for $2\theta = 5-40^\circ$.

Differential Scanning Calorimetry. The DSC (Figure S2) data were collected on a Mettler Toledo DSC 823e instrument with a heating rate of 5 °C per minute in a liquid nitrogen atmosphere.

Computation. Electrostatic potential surface maps were calculated for model bromoaromatics **5** and **6**. All the DFT calculations were performed in Gaussian 09 using B3LYP function and 6-311G (d, p) as basis set.⁶² Experimentally determined atom coordinates were used as input in Gaussian for each molecule. Compound **5** was prepared, and the crystal structure was determined in this regard. Coordinates for **6** were taken from the CSD. Electrostatic potential surfaces were obtained by molecular electron density 0.004 electron/Å. Color coding was used to locate positively charged (blue) and negatively charged surfaces (red).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11835.

Synthesis and crystallization, DSC diagrams, crystallographic information table, face indexing images, crystal packing of **2a**, **2c**, **2d**, **3b**, **4a-c**, and **4e**, representative synthons in 1D elastic **2a** and 2D plastic **4a**, crystal structure description, PXRD of **4d**, X-ray diffraction images before and after bending and image of a crystal of 1,4-dibromobenzene before and after butter paper supported twisting test (PDF)

Video S1, showing 1D elastic crystal of **2b** (form I) (AVI)

Video S2, showing 2D elastic bending of **3a** (AVI)

Crystallographic information file for **1**, **2a-d**, **3a,b**, **4a-c**, **5**, **B1**, and **E3** (CIF)

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Notes

The authors declare no competing financial interest.

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