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Elastic and Bendable Caffeine Cocrystals: Implications for the Design of Flexible Organic Materials**

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Dedicated to Professor Gautam R. Desiraju on the occasion of his 60th birthday

Molecular crystals are among the most ancient and highly investigated materials in chemistry. However, mechanical properties of these materials have remained relatively unexplored despite their unique applications in optoelectronics, mechanical actuators, artificial muscles, pharmaceuticals, and explosives.[1] Conserving the orientational order of molecules and bonds is important for efficient charge transport and for the lifetime of organic light-emitting diodes, transistors, and solar cells.[2] Hence, the realization of high-performance materials with excellent self-healing capabilities or efficient stress dissipating behaviors is attractive. For this reason, the remarkable properties displayed by natural fibres such as spider silk,[3] muscle protein titin,[1e,4] cytoskeleton microtubules,[5] etc. have recently sparked tremendous interest in establishing a reliable structure–property correlation to guide the design of their mimics for various applications. A good starting point for achieving such a goal is to study much simpler and easy-to-characterize organic crystals, which self-assemble through the same noncovalent interactions.

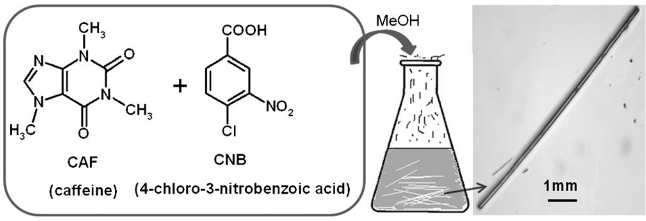

Figure 1. Single-crystal preparation of the cocrystal solvate **1** from a methanol solution of caffeine and 4-chloro-3-nitrobenzoic acid.

It remains a challenge to simultaneously achieve both flexibility and crystallinity in organic materials because crystallinity positively correlates with brittleness. For example, compared to highly ordered molecular crystals, liquid crystals show greater flexibility, but are less crystalline. Desiraju and co-workers showed irreversible mechanical bending in organic crystals as mediated by the movement of molecular sheets through weak interactions between them.[6,7] The plastic deformation disrupts the long-range order permanently. It was also shown that reversible molecular movements in organic crystals (e.g., in photomechanical bending), can perform work in devices.[8] Herein we report a remarkably flexible, elastically bendable cocrystal solvate **1**, formed from caffeine (CAF), 4-chloro-3-nitrobenzoic acid (CNB), and methanol in a 1:1:<1 ratio (Figure 1). The cocrystal solvate **1** retains a high internal order through an efficient stress dissipation mechanism, and hence is important in the context of crystal engineering[9] and for the design of flexible organic materials.

The single crystals of **1** could be obtained from a 1:1 molar solution of CAF and CNB in methanol by using a slow evaporation method (Figure 1).[10] ^{1}H NMR and thermogravimetric (TG) analyses have confirmed the presence of CAF, CNB, and methanol molecules in a 1:1:<1 ratio within the lattice (see Figures S1 and S2 in the Supporting Information). The typically long needle crystals of **1** grow along the *a* axis (Figure 1 and Figure S4). When a straight crystal, having about a 0.1 mm thickness and 5 mm length, was pushed with a metal pin while being held with a pair of forceps (tweezers) from the opposite end, it transformed into a bent shape without breaking (Figure 2a–d and Figure S5). Further, it could be made into a loop by joining the two ends with a smooth curve (see Videos S1–S3 in the Supporting Information). Upon withdrawal of the force, the crystal quickly

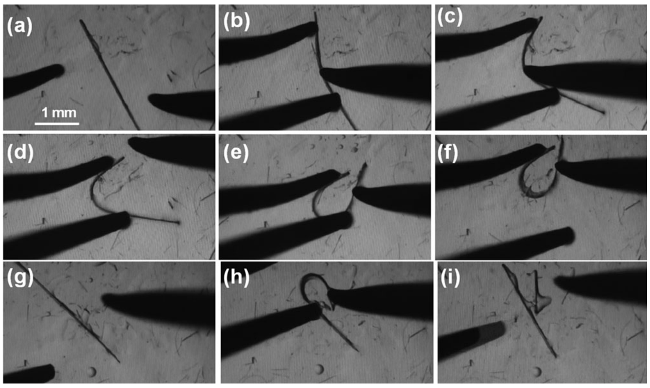

Figure 2. Elastic bending in the cocrystal solvate **1**. a–f) First bending cycle resulting from applied mechanical stress, using a pair of forceps and a metal pin. g) The subsequent recovery upon withdrawal of the force. h) Second bending cycle. i) The breaking of the crystal when the elastic limit is exceeded. Notice the remarkable shape recovery in the two broken halves in (i).

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regained the original shape without any sign of permanent deformation or cracks, thus revealing the highly elastic nature in **1** (Figure 2g). The bending cycles could be repeated many times. Use of fomblin oil or silicon grease helped to avoid any damage to the crystal from the metal devices. The crystal finally broke when it was pushed beyond a certain radius. However, the two broken halves underwent excellent shape recovery (Figure 2i). At $-100\,^{\circ}$C, the crystals were bent just as easily as they had been at room temperature (Figure S6). The very smooth curvature in the elastically bent crystal suggests a uniform distribution of the applied stress throughout the bent region. To our knowledge, such remarkable elastic bending is unprecedented in organic single crystals. Some metal–organic frameworks (MOFs) having a two-dimensional (2D) square-grid structure, interlocked in the third dimension by pillars, are known to display a high structural flexibility (expansion or compression of lattice).[11] Achieving high flexibility in fully organic materials is challenging as the construction of a stable host network is difficult because of the much weaker nature of the interactions involved. Consequently, long one-dimensional (1D) molecular crystals generally do not show such elastic bending. For instance, the crystals of form β for CAF (a parent compound of **1**), which are grown with comparable morphology, were easily broken by a gentle touch with a metal pin (Figure S8 and Video S4). This finding suggests that such morphology is not a sufficient condition and the crystal packing must be considered.

In pursuit of a structural basis for the elastic bending behavior, we determined the crystal packing of **1** by single-crystal X-ray diffraction (SCXRD).[12] Molecules in **1** cocrystallize in the orthorhombic polar space group *Fdd*2 with an elongated unit cell (Figure 3).[12] There is one molecule of CAF, one of CNB, and a highly disordered methanol molecule with partial occupancy (< 100%; see Figures S1–S3 in the Supporting Information) in the asymmetric unit. The disordered methanol could not be resolved satisfactorily because of the diffuse electron density in the cavity. Notably, the O atoms of the nitro group on CNB are also disordered over two out-of–the-molecular plane positions with equal occupancies, possibly a result of the steric hindrance from the adjacent Cl group.[13] CAF and CNB form dimers through a supramolecular synthon involving a strong O–H···N (d/Å, θ/°: 1.57(7) Å, 177(7)°) and a supportive C–H···O (2.62(9) Å, 119.2°) hydrogen bond (Figure 3c; see Table S1 in the Supporting Information). The CAF molecules of adjacent dimers join through another weak C–H···O (2.38(7) Å, 139(7)°) interaction to form comblike 1D tapes parallel to the *a* axis, that is, along the crystal length (Figure 3b). Molecules of these adjacent tapes stack to form thick 2D sheets in the *ac* plane. This leaves the CNB molecules from alternate dimers to fall onto either side of the 2D sheet, thus resulting in a double-sided comblike 2D sheet. The 2D sheets then pack in a zipperlike manner by bringing together the CNB molecules of opposite sheets through van der Waals forces (Figure 3b). Open channels, which are formed between the 2D sheets along the *c* axis, are occupied by disordered methanol molecules. The 1D tapes of two adjacent sheets (red and green lines in Figure 3e) make an angle of approximately 40° with each other. This arrangement is expected to cease the slippage of molecules when a mechanical stress is applied perpendicular to the readily bendable (010) face. The structure is nearly isotropic with the even distribution of weak interactions in all the three perpendicular directions, as also supported by the variable-temperature unit cell data (Figure S9).

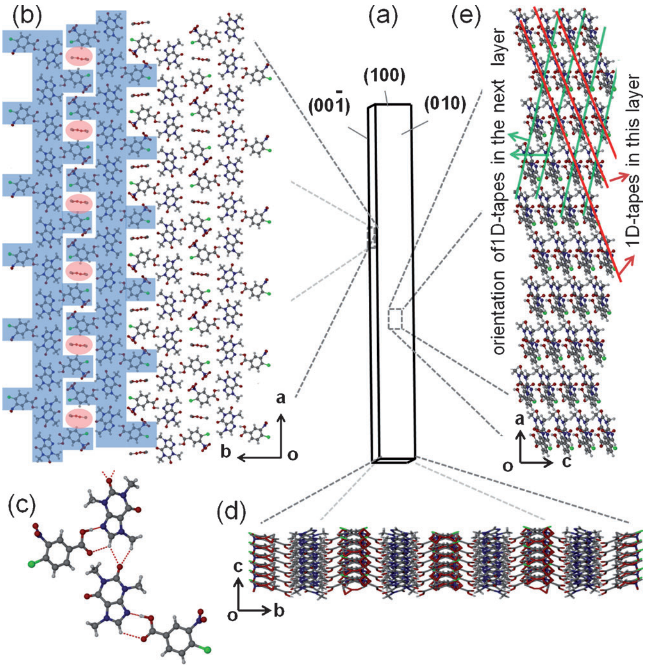

Figure 3. Crystal packing in **1**. a) Crystal morphology with face indices. b) Interlocking of the comblike 2D sheets (blue) and the formation of channels (red) with disordered methanol along the *c* axis. c) Formation of dimers by CAF and CNB through O–H···N and C–H···O interactions; the CAF molecules form 1D tapes. Views perpendicular to d) (100) and, e) the 2D layers in (010).

Further examination of the morphological features of the crystal before and after the mechanical bending in **1**, as well as the previously established plastic bending,[7] provided us with some key insights into the possible structural basis for the elastic bending (Figure 4). In the plastic bending 1) the presence of slip planes is a prerequisite; 2) angles between the crystal top and bending faces (θ) change markedly to preserve the original length (l_0) in the inner (l_{in}) and outer (l_{out}) arcs of the crystal (i.e., $l_0 = l_{\mathrm{out}} = l_{\mathrm{in}}$); and 3) bending is highly anisotropic, that is, crystals bend on a particular pair of faces, whereas they break on the second pair of faces, unless all the side faces are identical, such as in a highly symmetric crystal (Figure 4a).[7] However, in the case of the elastic cocrystal **1**: 1) there are no slip planes in crystal structure as evident from the visual inspection; 2) there is no readily detectable change of angle between the (100) top and bending face, hence the $l_{\mathrm{out}} \neq l_{\mathrm{in}}$; and 3) bending occurs elastically for both pairs of side faces, that is, (010)/(0−10) and (001)/(00−1).

Elastic bending without any changes to the interfacial angles ($\theta = \theta_0$) introduces the strain energy (Es) in the crystal as this requires stretching and compression of outer and inner arcs, respectively. Hence molecules on both the arcs must collectively move in a coordinated manner, but in the

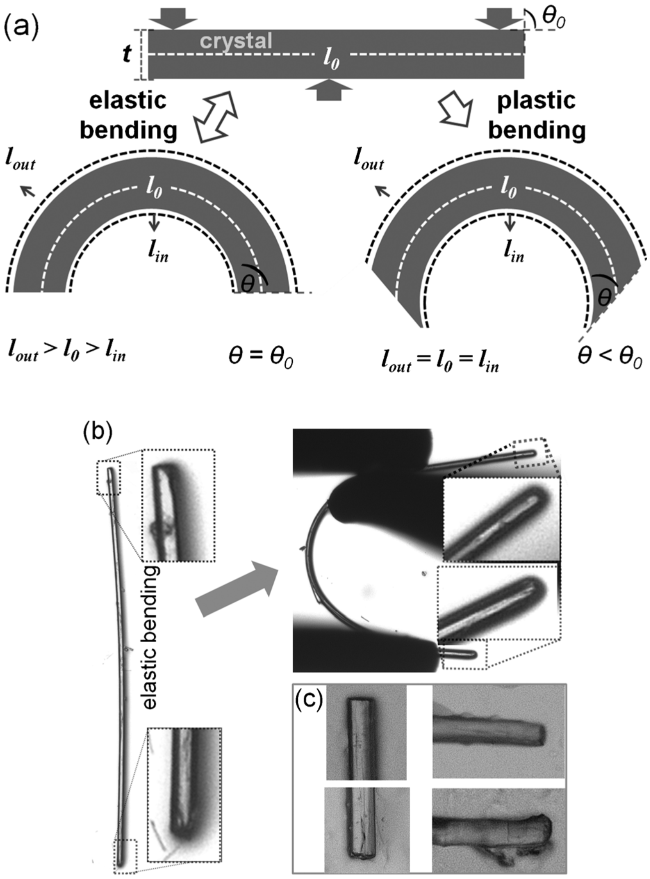

Figure 4. a) Schematic representation of the crystal before and after elastic (left) and plastic (right) bending. Notice the morphological differences at the crystal ends in the two cases. b) Stereo and c) polarizing micrographs of the crystal **1**. Comparison of the crystal ends, before (left) and after (right) the elastic bending of **1** into the semi loop in (b) or (c), shows the absence of any detectable changes to the interfacial angles.

opposite directions and away from their idealized thermodynamic positions. The energy surfaces of the path between the ideal and the delocalized (high energy) molecular positions must remain smooth with insignificant energy barriers. Molecules in halfway through the crystal shall remain close to their original thermodynamic positions, as the length at this region is not expected to change ($=l_0$), and is often referred to as the neutral axis.[14] Though the crystals bend on either of the two pairs of side faces, it is easier to bend the thinner pair (010)/(0−10). When the same pair is considered in different crystals, thinner crystals show a higher flexibility. For example, a crystal of 0.1 mm thickness (t) and 5 mm length (l_0) could easily be folded into a loop (360° of angle between two ends), whereas one with a 0.5 mm thickness and the same length ($l_0 = 5$ mm) could not be bent more than 90°. The thicker crystals will experience a higher Es as the magnitude of the change in length (Δl) of both arcs will be greater for the same extent of bending. The Es will also increase with the decrease in loop radius (r) as can be understood from continuum mechanics.[15,16]

A simple calculation for the above two crystals having different t values, provides a qualitative estimate for their Δl magnitudes. When a crystal is made into a full loop (not to be confused with the semiloop in Figure 4a), its perimeter along the neutral axis would be equal to the l_0, hence $r = l_0/2\pi$ (see Figure S10 in the Supporting Information). The r values for the inner (r_{in}) and outer (r_{out}) arcs would be $(r-t/2)$ and $(r+t/2)$, respectively. The magnitude of the Δl_{out} ($=l_{out}-l_0$) or Δl_{in} ($=l_0-l_{in}$) would be equal to πt (see the Supporting Information). For the first crystal, with $t = 0.1$ mm and $l_0 = 5$ mm, the $\Delta l_{out} = \Delta l_{in} = 0.314$ mm, and for the second crystal, with $t = 0.5$ mm and $l_0 = 5$ mm, the $\Delta l_{out} = \Delta l_{in} = 1.57$ mm. If the 0.314 mm of $\Delta l_{out/in}$ for the loop in the first crystal (i.e., the crystal in Figure 2) is distributed among the total number of molecules which are present in its 5 mm length on the (010) bending face, each CAF molecule in the 1D tape has to displace by 0.5147 Å along the crystal length, whereas this would be 2.57 Å for the thicker crystal ($t = 0.5$ mm). Although this is a qualitative estimate, it is clear that the magnitude of molecular movements in the latter case would introduce a severe strain in the noncovalent interactions on both the arcs. The bending limit (critical radius, r_c, for breakage) will be defined by the compressed arc and not by the elongated arc, because the compression of bonds is more difficult than expansion.[17] Hence the crystal breakage in the latter case is in good agreement. The r_c of the loop depends upon the length and thickness of the crystal. The crystal in Figure 2h is made approximately into a loop using only its half-length (0.25 mm), and breaks at about that stage, thus revealing its r_c as approximately 0.39 mm (i.e., ≈ 1.029 Å molecule^{-1}).

If the recovery upon withdrawal of mechanical stress is truly elastic, all the molecules shall regain their original thermodynamic positions. To evaluate this, we examined a bent crystal, mounted carefully on a nylon loop, using the SCXRD technique. A number of diffraction spots, elongated in a certain direction (Figures 5a,b), as well as normal spots were observed. The fact that it did diffract confirms that the periodic nature of the crystal is largely retained in the bent state. The elongation of spots signifies the localized movement of molecules away from their idealized lattice points, that is, stretching or compression of molecules through noncovalent interactions. However, the diffraction spots from the bent crystal could not be indexed to the original unit cell. When the crystal relaxed it produced sharp diffraction peaks which could be indexed to those of the original unit cell with standard deviations comparable to that of the undeformed crystal (Figures 5c,d; see Table S2 in the Supporting Information). This data confirms the exceptional elastic (i.e., fatigueless) nature of the crystal **1** at the microscopic level. The possibility of slippage or the large translational movements by molecules can be safely excluded in this case as such mechanisms do not favor the spontaneous recovery in crystals.[6b] For example, in the plastic shearing or bending, the slippage by weak interaction planes leads to irreversible molecular movements, that is, no recovery.

To evaluate the role of solvent in the elastic behavior, the differential scanning calorimetry (DSC) and TG analyses were carried out on **1** (see Figures S11a,b in the Supporting Information). This analysis showed the loss of solvent at 115 °C with subsequent melting at 135 °C. Heating the crystals in an oven at 60 °C for about 10 minutes also resulted in the

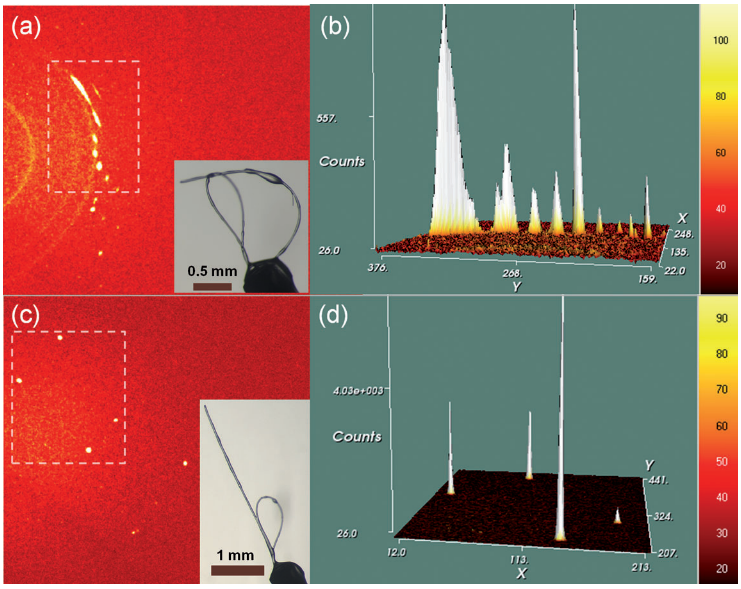

Figure 5. a) Bruker diffraction image (exposure time = 50 s), obtained from a crystal mounted in the bent shape on a nylon loop (inset). b) 3D view of the area marked in (a) shows a significant elongation of the reflections. c) The excellent shape and intensities of the diffraction spots from the relaxed crystal (inset) depicts the conservation of long range order in the elastic crystal. d) 3D view of the area marked in (c).

complete loss of the solvent, as confirmed from DSC. The dried cocrystals [**1**(dry)] showed a very similar PXRD pattern (except some small differences) and Raman intensities (Figures S12 and S13), thus suggesting that the lattice did not collapse upon escape of the methanol. Surprisingly, the crystals of **1**(dry) did not show any elastic property, but broke easily under the applied stress. As **1**(dry) could not be resolvated, it did not regain its elastic property. This data confirms that the presence of solvent in channels is required for the elastic bending. Interestingly, the crystals of **1**(dry) prepared from the crystals of **1** in the bent state (trapped in the bulk) remained in the bent shape even after they relaxed. In an attempt to straighten them by using mechanical stress, the crystals simply broke (Figures S11c,d; Video S5), thus revealing the unique thermosetting nature in **1**.

From the above experiments it is clear that the molecules on the outer arc will stretch while those on the inner arc will get compressed. If we consider the packing on the thinnest face (010), the CAF molecules that form 1D tapes through weak C−H⋯O interactions are nearly along the *a* axis, that is, the crystal length (Figure 3). These tapes further pack through the weak π-stacking interactions along the *c* axis to form 2D sheets parallel to the crystal face (010). As the interactions along both these directions in (010) plane are weak, their rearrangement/disruption is not expected to be adverse as this does not cause a steep energy rise in the structure (because of their dispersive nature and low specificity). When bending on the (010) face, the length of the C−H⋯O interactions between the CAF molecules in the 1D tapes probably increases on the outer arc, while decreasing on the inner arc. The CAF molecules also need to tilt with respect to each other to accomplish the crystal's bend angle, thus leading to the angle strain. The suggested molecular motions demand only a minimal rearrangement of π-stacking interactions within the 2D sheets (i.e., they do not destabilize the structure). Moreover, the criss-cross arrangement of the tapes from adjacent 2D sheets (Figure 3e) and comblike locking of the layers help to prevent slippage and thus hinder the large molecular movements. When the stress is released, the crystal regains the original structure by reversal of the molecular movements, which are only minimal. Similarly the bending on a thicker pair of faces (001)/(00−1) may also be understood based on the same weak interactions. The loss of elasticity in **1**, upon drying, is likely due to the introduction of defects to the crystals of **1**(dry). The site of the defect can then concentrate stress and cause premature breakage. The solvent molecules probably act as rollers between the comblike 2D sheets, while the π-stacking interactions do the same job in the other direction, but further studies are needed to assess this.

In conclusion, we showed the elastic mechanical bending and excellent shape recovery in the cocrystal solvate **1**, formed from caffeine, CNB, and methanol. Analysis of the results suggests an interlocked host structure with no slip planes, as well as weak and dispersive interactions in the three perpendicular directions and mobile solvent channels, which is probably responsible for the high flexibility in **1**. The excellent conservation of long-range order in both the bent and recovered crystals is important in the context of crystal engineering with implications for the design of high-performance flexible materials. The realization of dynamic crystalline organic nano/microstructures with the ability to conserve the orientational order of π-conjugated molecules will be of immense importance for efficient charge transport or propagation of light in the optoelectronic materials for device applications.[18] Crystals of organic functional materials with such an elastic nature may find unique applications, including flexible 1D waveguides, flexible ion channels, and flexible photovoltaic materials. The present study also demonstrates the ability of small molecular materials to display the remarkable elastic properties which have only been observed in complex biomaterials and polymers. Additional studies on more examples may ultimately provide some valuable insights for the design of flexible and high-performance engineering materials.

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