Structural basis for bending of organic crystals†

**C. Malla Reddy,[a] Ravi C. Gundakaram,[b] Srinivas Basavoju,[a] Michael T. Kirchner,[a]
K. Anantha Padmanabhan*[c] and Gautam R. Desiraju*[a]**

Received (in Cambridge, UK) 12th April 2005, Accepted 23rd May 2005
First published as an Advance Article on the web 23rd June 2005
DOI: 10.1039/b505103g

Bending is observed in organic crystals when the packing is anisotropic in such a way that strong and weak interaction patterns occur in nearly perpendicular directions.

The typical organic crystal is not mechanically robust and is susceptible to deformation or breakage on application of stress.[1] We report here the phenomenon of bending of organic crystals. While evidence for such a phenomenon might be anecdotal, and surely crystals with unusually deformed morphologies have been noted by crystallographers over the years, we are unaware of any report that systematically correlates such bending with crystal packing and intermolecular interactions. When a crystal bends, two parallel opposite faces become non-planar. We define these as the bending faces and the crystal bends when it is subject to a mechanical stress perpendicular to this pair of opposite faces. Other crystal faces must also undergo some deformation during bending but generally will not lose planarity.

We first observed this phenomenon in a survey of around 60 crystals with a short crystal axis of *ca.* 4 Å;[2] around 15 of them could be bent. A good example is 2-(methylthio)nicotinic acid, **1**, the crystal structure of which we recently determined.[3] The packing (Fig. 1d) consists of acid dimers stacked down the needle direction [100], which is the short axis. The dimers are arranged laterally along [001] with C–H$\cdots$O interactions. Along the third direction, namely [010], adjacent dimers are close packed with Me$\cdots$Me contacts. The bending of **1** is illustrated in Fig. 1c. A platelike crystal, which was placed on a slide so that the (001) face was on the top, was prevented from movement at its ends on $(0\bar{1}0)$ by a pair of forceps. Pressure was then applied with a needle from the other side of the crystal, that is on (010), and in the middle. The crystal bent easily as seen in Fig. 1c. This bending could be continued till the crystal assumed a hairpin shape. We noted that this bent crystal could also be 'straightened out' somewhat with the sites of the instruments reversed (forceps ↔ needle) but that it did not regain its pristine condition: mainly, it no longer showed the diffraction characteristic of a single crystal. Bending is strongly anisotropic in these crystals. When a crystal of **1** was placed with the (010) face upwards, and subjected to mechanical stress but with the needle and forceps coming in on the (001) and $(00\bar{1})$ faces, it cracked and eventually broke.

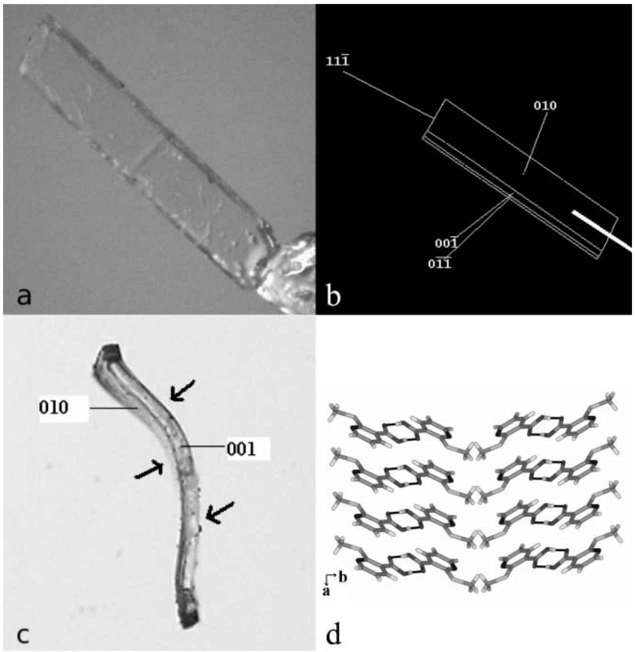

Fig. 1 2-(Methylthio)nicotinic acid, **1**. (a) Crystal as mounted for face indexing. (b) SMART face indexing graphic. (c) The same crystal bent on the (010) face; arrows show the point of impact of forceps and needle. (d) Crystal packing shown in the same orientation as (c). Notice the weak Me$\cdots$Me interactions and $\pi\cdots\pi$ molecular stacking.

A schematic depiction (Fig. 2) shows the crystal structure as viewed on the (001) face. The acid dimers in the undeformed crystal (Fig. 2a) are shown as stacked disks, and the white regions between the molecular stacks correspond to Me$\cdots$Me close packing. For bending of the kind observed, one set of interactions ($\pi\cdots\pi$ stacking) should be substantially stronger than another (Me$\cdots$Me van der Waals) in a nearly perpendicular direction. Application of mechanical stress would then lead to the situation shown in Fig. 2b. We suggest that the disks are able to assume their distorted orientations in the bent crystal either by sliding along the molecular planes or splaying (see the change in orientation between the black disks in Fig. 2).

A nanoindentation test revealed that the Young's modulus of crystal **1** ($\sim$15 GPa) was comparable to that of wood.[4] It could also be demonstrated that, at room temperature, crystal **1** experienced steady state creep (Fig. 3, inset). In this experiment, the load was maintained constant; yet the depth of indenter penetration increased with the time of load application. This is constant load

---

[a] *School of Chemistry, University of Hyderabad, Hyderabad 500 046, India. E-mail: gautam_desiraju@yahoo.com; Fax: +91 40 23010567; Tel: +91 40 23134828*
[b] *International Advanced Research Centre for Powder Metallurgy and New Materials, Balapur P.O., Hyderabad 500 005, India*
[c] *School of Physics, University of Hyderabad, Hyderabad 500 046, India. E-mail: ananthaster@gmail.com; Fax: +91 40 23011777; Tel: +91 40 23011777*

† Electronic supplementary information (ESI) available: list of 15 organic crystals which bend easily and relevant crystallographic information for them. See http://www.rsc.org/suppdata/cc/b5/b505103g/index.sht

(~stress) indentation creep.[5] Creep becomes significant in a material when the test temperature is greater than or equal to 0.5 T_{m}, where T_{m} is the melting point.[5a] Here the test temperature was 298 K, while the mp of **1** is 488 K. That the interactions in crystal **1** are quite anisotropic could also be demonstrated by the nanoindentation experiments in which the hardness of the crystal at different values of indenter penetration along the three crystal directions was determined. Fig. 3 shows that the hardest face is the bending face, (010). This is because application of a mechanical stress perpendicular to this face causes the rest of the crystal to deform plastically.

A consequence of our model is that the angles between some of the faces would change markedly. In **1**, for example, the angle between (11$\bar{1}$) and (010) would become much more acute as the crystal deformed. This is not very clear in **1**, but a similar effect is observed very prominently in the bent crystal of pyrazinamide, **2**, (Figs. 4a and 4b) which is also distinctive in that the thin face of the crystal, (100), is the bending face (Figs. 4d, 4e and 4f). The crystal packing of **2** (Fig. 4c) is similar to that of **1**. There is a 4 Å short axis, a stacking of amide dimers along this axis and weak, non-specific interactions between phenyl rings along another. Again, one set of interactions (stacking) is significantly stronger than another (Ph$\cdots$Ph) in a perpendicular direction. Bending, therefore, is a consequence of the crystal packing and does not depend on morphology. For example, it is not that the largest area faces of a crystal are the bending faces (as in **1**). In **2** we see that the bent crystal cracks rather than bends along a prominent face like say, (2$\bar{1}$0).‡ Interestingly, amide **2** is polymorphic.[6] We could crystallize forms α and δ, and our experiments above pertain to the former; the latter could not be bent under similar conditions.

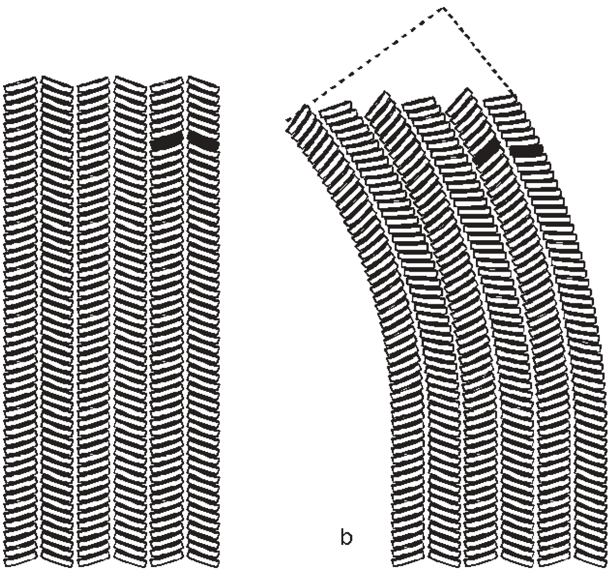

Fig. 2 A model for bending (half sectional view). (a) Undeformed crystal. The white spaces between rows of stacks represent the weakest interactions. (b) Bent crystal. Note the pronounced change in some of the interfacial angles.

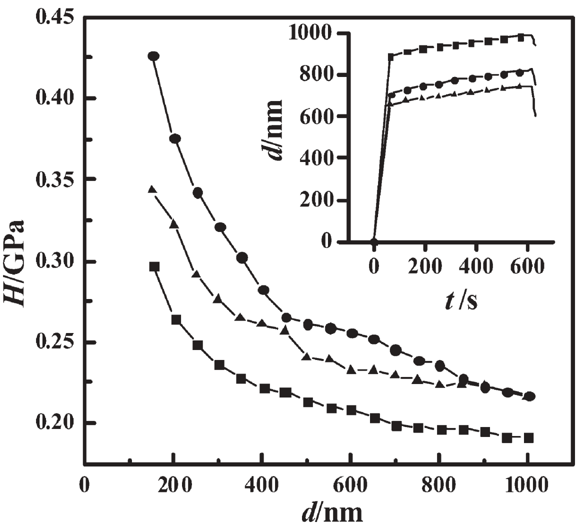

Fig. 3 Nanoindentation experiments demonstrating anisotropy in acid **1**. Hardness *vs*. depth of indenter penetration. Inset: Indenter penetration *vs*. time of load application. ▲ (100), ● (010), ■ (001).

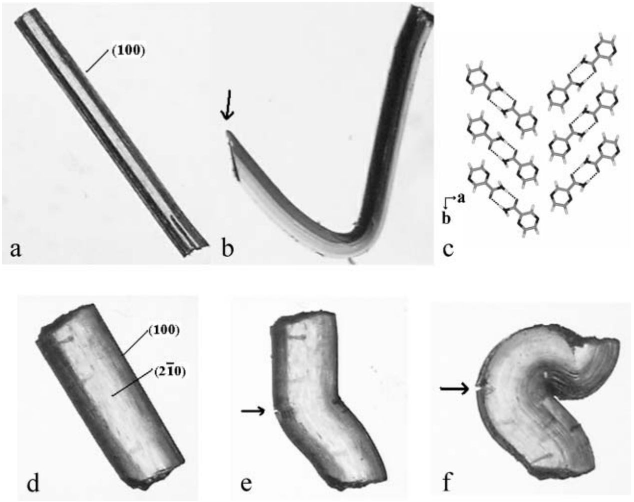

Fig. 4 Pyrazinamide, **2**. (a) Before bending. (b) After bending. The arrow shows the acute interfacial angle. (c) Crystal packing. (d), (e) and (f) show the stages of bending on the (100) plane on another crystal. Arrows in (e) and (f) indicate points of breakage.

Other examples confirm our model. In hexachlorobenzene, **3**, (mp 500 K) the bending face is (001) and is where the weak and non-specific Cl$\cdots$Cl contacts emerge (Fig. 5b). The isostructural hexabromobenzene, **4**, (mp 598 K) did not bend, and this

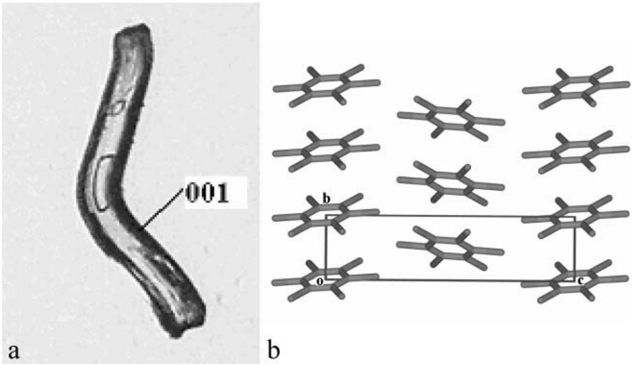

Fig. 5 Hexachlorobenzene, **3**. (a) Crystal bent on (001) face. (b) Packing diagram.

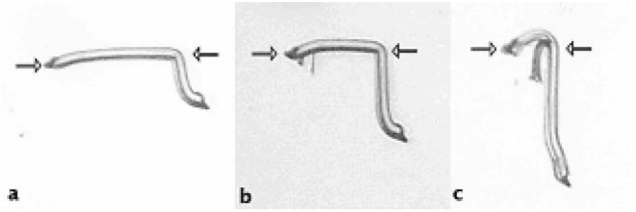

Fig. 6 Hexachlorobenzene, **3**. (a), (b) and (c) show the propagation of the bend through the crystal on continuous stress application. Arrows show the point and direction of the stress applied.

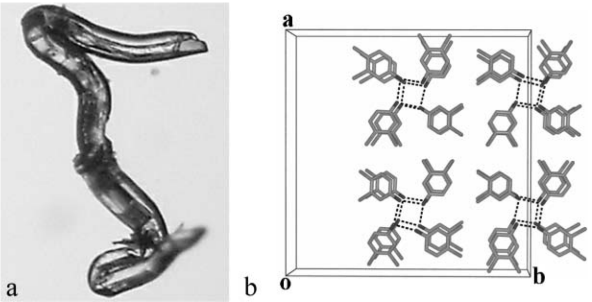

Fig. 7 3,4-Dichlorophenol, **5**. (a) Crystal bent to sides, up and down. (b) Packing diagram.

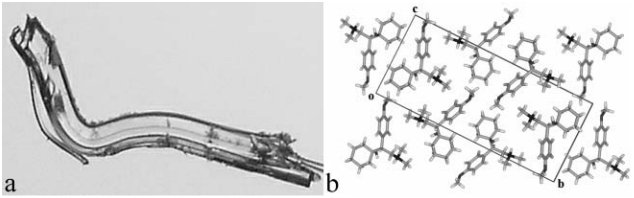

Fig. 8 Venlafaxine hydrochloride, **6**. (a) Crystal bent on (010) face. (b) Packing diagram.

appeared counter-intuitive. However, using the well known idea that the best way of comparing the mechanical response of materials is in terms of similar homologous temperature[5a] (equal to T/T_m, where T is the temperature of deformation), we repeated the bending experiment at 403 K. Bending occurred as it did for **3** at room temperature. An interesting sidelight here is that the bend in the crystal propagates when the stress is suitably applied on the sample (Fig. 6).

In the tetragonal 3,4-dichlorophenol, **5**, the stacking interactions are along the unique direction (Fig. 7b).[7] The much weaker Cl···Cl directions are equivalent along the two other perpendicular directions because of crystal symmetry. Therefore, **5** bends into a variety of shapes (Fig. 7a). For such high symmetry crystals, more than one pair of faces are bending faces. Finally, venlafaxine hydrochloride, **6**, has a one-dimensional packing with strong, ionic interactions in one direction, [100] and van der Waals packing elsewhere (Fig. 8b).[8] These crystals bend on the expected (010) faces. Salt **6** is currently important in the pharmaceutical industry and exists as two polymorphs.[9] One bends and one does not. This is not a 4 Å structure and shows that aromatic ring stacking is not mandatory for bending. The supplementary information contains a list of other crystals which bend easily.† In all these cases, the necessary and sufficient condition for bending is that there should be one strong interaction pattern and a much weaker one in a perpendicular direction.

In summary, bending of organic crystals is a widespread phenomenon. It can be understood on the basis of a structural model that takes into account the highly anisotropic nature of these crystals. An organic crystal which bends is not like plasticine, modelling clay or even a slab of metal. It cannot be mechanically deformed in any arbitrary manner. Interactions in such crystals are not uniform and similar in all directions. Isotropic crystals, wherein the packing patterns are similar in three dimensions, will often have highly cross-linked structures (naphthalene, benzoic acid, D-glucose). These crystals would break rather than bend when subjected to a mechanical stress. In contrast, metals, which are isotropic but do not have cross-linking, display excellent plasticity. Mechanical properties of molecular crystals are important because they have major implications for processing and handling of materials in industry. Soft crystals become pasty upon grinding. Harder crystals are granular and can be handled more easily. Plastic deformation of a solid may also affect its chemical properties.[10] A further assessment of these undoubtedly common but little understood properties is clearly desirable.

CMR and SB thank the CSIR for SRFs. RCG thanks G. Sundararajan and R. Sundaresan for their encouragement. MTK thanks the AvH Foundation for a Lynen Fellowship. GRD thanks the DST and DRDO for financial support of his research. DST provided the CCD diffractometer under the IRPHA programme.

Notes and references

‡ But cracking always starts in the region of maximum tensile stress.

1 (*a*) J. D. Wright, *Molecular Crystals*, Cambridge University Press, Cambridge, 1996; (*b*) A. R. West, *Solid State Chemistry and its Applications*, Wiley, Chichester, UK, 1984, pp. 347–351; (*c*) P. Pavlides, D. Pugh and K. J. Roberts, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1991, **A47**, 846; (*d*) G. M. Day, S. L. Price and M. Leslie, *Cryst. Growth Des.*, 2001, **1**, 13.
2 C. M. Reddy, S. Basavoju and G. R. Desiraju, *Chem. Commun.*, 2005, 2439.
3 S. Basavoju, C. M. Reddy and G. R. Desiraju, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2005, **E61**, o822.
4 M. F. Ashby and D. R. H. Jones, *Engineering Materials*, Pergamon, Oxford, 1980, p. 31.
5 (*a*) G. E. Dieter, *Mechanical Metallurgy*, McGraw-Hill, Singapore, SI Metric edn., 1988, pp. 301 and 433; (*b*) K. A. Padmanabhan, P. Mondal and H. Hahn, *J. Mater. Sci.*, 2005, in press.
6 (*a*) Y. Takaki, Y. Sasada and T. Watanabe, *Acta Crystallogr.*, 1960, **13**, 693; (*b*) G. Ro and H. Sorum, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1972, **B28**, 991; (*c*) G. R. Desiraju, *Science*, 1997, **278**, 404.
7 (*a*) N. W. Thomas and G. R. Desiraju, *Chem. Phys. Lett.*, 1984, **110**, 99; (*b*) C. Bavoux, M. Perrin and A. Thozet, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **B36**, 741.
8 (*a*) A. Sivalakshmidevi, K. Vyas, S. M. Rao and G. O. Reddy, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **E58**, o1072.
9 D. Vega, D. Fernandez and G. Echeverria, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **C56**, 1009.
10 V. V. Boldyrev, *Reactivity of Solids: Past, Present and Future*, Blackwell, Oxford, 1996, p. 272.