CHAPTER 2

SHEARING, TWINNING AND ANISOTROPY IN LAYERED MOLECULAR STRUCTURES

2.1 Introduction

The forces that bind atoms into crystalline solids are electrical in nature, and in the broadest sense, can be termed as chemical bonds. There are five principal chemical bond types: metallic, ionic, covalent, hydrogen bond and van der Waals [2.1, 1.2]. Each bonding type is characterized by its particular strength and directionality characteristics. To a great extent, the bonding type determines the physical and chemical properties of a solid material at a given temperature [2.2]. For instance, hardness, cleavage, thermal and electrical conductivity are directly related to chemical bonds. Based on the directionality of chemical binding forces in crystalline state, solids are classified into 0D, 1D, 2D and 3D [2.3]. Among these types the 3D solids are well documented. Comparatively speaking, detailed studies of 2D solids are not so common [2.4]. Dimensionality is one of the most defining of material parameters: the same chemical compound can exhibit considerably different properties depending up on whether it is arranged in a 0D, 1D, 2D or 3D crystal structure [2.3, 2.4]. For example, the three allotropes of carbon—buckminsterfullerene, graphite and diamond—provide a potent example of how much the structure and properties of a system can vary with dimensionality [2.5b]. Buckminsterfullerene, a 0D molecular crystal, is very soft. In graphite, the weak van der Waals interactions that hold the trigonally bonded two-dimensional carbon layers together make it soft enough to cleave the material along these layers. In diamond, the carbon atoms are extended three-dimensionally by strong tetrahedrally directed covalent bonds of length 1.54 Å that makes it the hardest material in nature [2.3].

2.2 Overview of Two-Dimensional Structures

There are many kinds of layered structures in the literature with strong in-plane bonds and weak van der Waals interactions between layers. Sheets of layered crystals are
generally formed via metallic, ionic, covalent, hydrogen bonds and/or van der Waals interactions [2.3, 2.6]. The stacking of layers is simple, because of the small number of possibilities that exist. Other features like polytypism, polymorphism, disorder and cleavage of layers, occur due to variations in these basic stacking patterns such as the fcc (ABCABC) and hcp (ABAB) stackings. Variations in these simplest arrangements occur because of the weakness of the interlayer interactions [2.3].

2.2.1 Structure of Graphite and BN

The classic example for covalent crystals with a distinctive layered structure is carbon in graphite, wherein intralayer bonds are formed via sp² hybrids exactly as in benzene. In this structure, the layers are formed with atoms, connected to these three nearest neighbours with covalent bonds, Figure 1. π-Orbitals normal to the plane overlap to form π-molecular orbitals covering the entire layer. The layers are widely separated with a perpendicular distance of 3.35 Å and bonded by van der Waals forces only. Due to the weakness of interlayer interactions, graphite is readily cleaved and hence, used as a heavy-duty lubricant and ‘lead’ in pencil. Because of its interesting structural arrangement and the shearing behaviour of its layers, graphite has been investigated extensively and has been found to be useful in many ways [2.3].

![Figure 1. The layered structure of hexagonal graphite.](image-url)
Any two graphite layers can be stacked in only one way, viz. with three alternating atoms of one ring above ring centres in the lower layer, Figure 1. The third layer can either be above the first (ABAB, giving hexagonal graphite) or displaced with respect to it (ABCABC, rhombohedral graphite). However, the ABC stacking is never found to extend throughout any one crystal; a complex form of disorder is present.

Planar layers of the same kind are also present in white BN, the isoelectronic solid which is dimorphic analogous to carbon [2.3]. Alternate boron and nitrogen atoms occur in graphite-like rings in BN but the layer stacking is not the same (Figure 2) and must result from weak directed bonding via \( p \)-orbitals normal to the layers. The higher electronegativity of nitrogen results in a greater delocalization of \( \pi \)-electrons than in graphite: consequently BN is an insulator. At high temperature and pressure (40 kbar) white BN transforms to a cubic form with the diamond structure and greater hardness.

![Figure 2. The layered structure of hexagonal BN.](image)

Very recently, Novoselov et al. have reported free-standing atomic crystals that are strictly 2D and can be viewed as individual atomic planes pulled out of bulk crystals or as unrolled single-wall nanotubes [2.4]. They have taken several samples of layered materials with very strong intralayer bonds namely, graphite, BN, MoS\(_2\), NbSe\(_2\) and Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_x\), and obtained atomic 2D crystals by rubbing a fresh surface of the crystal against another solid surface, which left 2D atomic crystals along with a variety of other flakes. These atomic crystals were primarily identified by viewing the flakes on top of an oxidized Si wafer under the optical microscope and further investigated using scanning
tunneling, scanning electron, atomic force microscopy (AFM) and high resolution transmission electron microscopy (HRTEM). Electric field effects of few atomic thick carbon films were also studied by this group of scientists [2.7].

2.2.2 Structure of CdI₂

CdI₂ is termed a ‘layer structure’ because it consists of repeat units (sandwiches) \text{I}–\text{Cd}–\text{I}…\text{I}–\text{Cd}–\text{I}…\text{I}–\text{Cd}–\text{I} (where the symbols Cd and I represent layers of those atoms) with contact between adjacent iodine layers (Figure 3) [2.3]. CdI₂ is trimorphic. The known structures differ in the layer-stacking sequence (ABAB, ABCB or ABAC, and ABCACB). This is clearly not an ionic structure; bonds to the metal will be semi-ionic, but the I⋯I attraction is principally of the van der Waals type. Accordingly, the structure is easily cleaved between the I⋯I planes, which accounts for the flaky nature of the crystals. Much work has been done in the structural characterisation of the CdI₂ polytypes [2.8]. The related CdCl₂ structure has a cubic close packed stacking of layers (ABCABC) and the anisotropic properties are similar.

![Figure 3. (a) The hexagonal CdI₂ structure. (b) The coordination around one I-atom.](image)

2.2.3 Structure of B(OH)₃

Orthoboric acid is a dimorphic compound and both forms adopt layered packing [2.3]. In both the cases, the sheets are formed by the pseudo-hexagonal nearly perfect \text{C}_{3\text{h}} symmetrical B(OH)₃ molecules, which are connected \text{via} O–H⋯O hydrogen bonds to
three adjacent molecules (Figure 4). Hydrogen bond metrics in both forms are nearly the same. In both cases the sheets are connected via van der Waals interactions. However, the stacking sequences of the sheets differ between the two polymorphs. In $\text{H}_3\text{BO}_3-3T$ (space group $P3_2$), the sheets are stacked with the repeating sequence ABCABC, whereas in $\text{H}_3\text{BO}_3-2A$ (space group $P-1$), the sheets are stacked in the repeating sequence ABAB [2.9]. In effect, these structures are ccp and hcp variations of the same layer structure.

![Space filling model of pseudo-hexagonal sheet in B(OH)$_3$-3T formed via O─H···O hydrogen bonds (a) and molecular diagram of sheets (b). The sheet in the 2A polymorph is nearly identical.](image)

**Figure 4.** Space filling model of pseudo-hexagonal sheet in B(OH)$_3$-3T formed via O─H···O hydrogen bonds (a) and molecular diagram of sheets (b). The sheet in the 2A polymorph is nearly identical.

### 2.2.4 2,4,6-Triethynyl-1,3,5-triazine

The crystal structure of 2,4,6-triethynyl-1,3,5-triazine, recently reported by Ohkita et al., is a unique two-dimensional hexagonal network [2.10]. Weak C(sp)–H···N hydrogen bonds play a dominant role in stabilizing the layer structure, which is regarded as a supramolecular analogue of the hitherto unknown graphyne network. The network involves two types of short C(sp)–H···N contacts and has a head-to-tail polar tape using the first of these contacts. The tapes are connected to each other through the second of these contacts to form a polar network, which is stacked in an antiparallel fashion (Figure 5) at a separation 3.23 Å.
Figure 5. Two dimensional hexagonal network structures of (left) graphyne and (right) supramolecular graphyne. The two short C(sp)–H···N contact types are marked 1 (polar tape) and 2 (linker between polar tapes).

2.3 Shearing in Metal Single Crystals by Mechanical Stress

Mechanical shearing [1.11, 1.18] is often observed in metals because it is easy to slide one layer of the crystal over the next. Shearing caused by the sliding of layers held by non-specific interactions may be seen in single crystals of metallic Cu [2.11]. However, Cu is completely isotropic and the plane of shearing is immaterial. Shearing occurs if two layers of a crystal are subjected to a shear stress greater than the yield stress of the material, as shown in Figure 6a. Although it appears that the whole layer shifts over the hump one notch to the next, this does not happen in actuality. Shearing of a crystal in such a way would require much more force than what is normally applied. It is believed that the mechanism of such shearing is cooperative. One atom moves at a time; first, the atom on the left makes its jump, then the next, and so on, as indicated in Figure 6b. In effect it is the vacant space between two atoms that quickly travels to the right, with the net result that the whole second layer has moved over an atomic spacing. The slipping goes this way because it takes much less energy to lift one atom at a time over the hump than to lift a whole row. Once the force is enough to start the process, it goes the rest of the way very fast. In a real crystal, slippage will occur repeatedly at one plane, and then start at some other plane. Figure 6c shows a photograph of a tiny, thin copper crystal that has been thus sheared and stretched.
2.4 Mechanically Induced Molecular Migrations in Layered Molecular Crystals

While dealing with solid state photochemical reactions, Schmidt proposed a topochemical hypothesis of ‘minimal atomic and molecular movements’ to explain the solid state reaction mechanism [1.7]. According to his hypothesis, molecules or atoms of the reactants have to move a minimum amount (at most 1.5 to 4.2 Å) to achieve the required topology (geometry, conformation and configuration) for the reaction to take place in the solid state. Schmidt’s topochemistry hypothesis denies large scale molecular migrations both for homogeneous and heterogeneous solid-state reactions.

In connection with Schmidt’s topochemical hypothesis, Kaupp et al. [2.12] have recently studied the action of mechanical stress [2.13] on two kinds of organic molecular crystals (layered and interlocked packing) by a new technique of nanoscratching at various faces in different directions in order to induce far-reaching anisotropic long-range molecular migrations. These workers have correlated their results with crystal packing and topochemical reactivity [2.12, 2.14]. In these experiments mechanical
scratching on the flat face of a crystal was done using a vertical cube corner indenter (Berkovich indenter). The three sided pyramidal tips were aligned with the sharp edge in front or back accordingly. In these experiments, chemically reactive crystals of thiohydantoin, anthracene, thiourea, tetraphenylethene and ninhydrin experience anisotropic long-range molecular migrations within the crystal because they exhibit cleavage planes between mono- or bi-layers along which migration occurs. For instance, thiohydantoin is an almost planar molecule with many hydrogen bonding acceptors and donors. It crystallizes in monolayer sheets that are 66° skew under the natural (110) face with cleavage planes between them. Scratching experiments in four different orthogonal directions on the skew cleavage planes of the crystal gave molecular migration (shift of debris) to different sides (Figure 7). The sketch in (a) and (d) of Figure 7 visualizes this situation more clearly. At 0° (along the long crystal edge [001]) molecular migration is to both sides and in front (b); the cracks indicate the direction of the cleavage planes. At 90° molecules migrate only to the right hand side (c). Only scratch (or abrasion) is detected at 180° as the tip moves against to the skew monolayers debris penetrate into the cleavage planes (e). At 270° molecules migrate only to the left hand side (f). The unusual piling-up of material only at one side of the scratch (Figure 7c, f) must be caused by the skew cleavage plane under the (110)-face. The geometric arrangement is such that the cleavage planes are open to the right side and blocked to the left side and vice versa as the scratching tip advances down in (b) and (d), respectively.

As there are multiple hydrogen bonds between the thiohydantoin molecules within a layer, single molecules cannot migrate, rather it appears likely that small molecular aggregates, such as almost planar hexamers that are present in the crystal structure as cyclic entities, may be small enough for the migration. On the other hand, scratching cannot induce molecular migrations in the case of chemically unreactive crystals of 2-benzylidenecyclopentanone or cis-1,2-dibenzylethene which are packed with 3D-interlocking (Figure 8). Sometimes shift of debris in front or only abrasion is seen in these cases.
Figure 7. Nanoscratching on the (110) face of thiohydantoin crystals. Schemes (a) and (d) show the geometric conditions of the skew sheets sloping to the right and left respectively. AFM topographies of 5 mm nanoscratches with a cube corner at 250 mN in 60 s; (b) 0º, (c) 90º, (e) 180º, (f) 270º orientation with respect to the long crystal edge [001] or stacking direction. This figure is taken from reference [2.12a].

Figure 8. 2-benzylidenecyclopentanone (3D-interlocked packing); 15 mm AFM topography on (010) after ramp scratching with a cube corner indenter at 0–150 mN in parallel (a) and orthogonal (b) directions with respect to the long crystal edge [010], showing only abrasion and some debris collection in front. This figure is taken from reference [2.12a].
2.5 Results and Discussion

This chapter deals with the mechanical shearing, twinning and anisotropy of the layered structures 135B246I-T, 135C246I, 135B246M, 135I246M, and the molecular complexes 135C246I:135B246I, 135C246I:135I246M, 135C246I:135B246M, 135B246I:135I246M, as also 6-chloro-2,4-dinitroaniline 1 and 4-bromoacetophenone, 2 (Scheme 1).

Crystals of 1,3,5-Trichloro-2,4,6-triiodobenzene, 135C246I provides a good example for shearing crystals. 135C246I crystallizes from THF in the triclinic, \( P \overline{1} \) space group as long and thick blocks [2.15]. Molecules in its crystal structure are arranged in planar layers parallel to (100) and in a nearly hexagonal arrangement with clusters of three I-atoms from three neighboring molecules and correspondingly, clusters of three Cl-atoms (Figure 9). The I₃ clusters are formed with short I···I contacts within van der Waals distance. The Cl₃ clusters have Cl···Cl contacts somewhat loosely packed because of the bigger size of the I₃ clusters. These intralayer I···I interactions are chemically significant, because they are formed by polarization of I-atoms, which make the planar sheet strong. Successive planar layers are inversion related and stacked so that bumps in one layer fit into the hollows of the next. The interlayer interactions are non-specific in
that they are based on close packing of spheres in hollows. The planar layer structure in 135C246I is reproduced in the corresponding bromo derivative 135B246I-T, and in the methyl derivative 135I246M [2.16], 135B246M and 135C246M. Mechanical properties of these crystals are discussed in this chapter while the detailed crystal structure analysis will be discussed in Chapter 5, noting the implications of these results on my understanding of the nature of halogen···halogen interactions.

Figure 9. Crystal structure of 135C246I. (a) Top view of a layer and (b) side view of layers.

Scheme 2. Mechanical shearing of a layered structure using a needle and forceps.

Crystals of 135C246I, grown from THF by slow evaporation, were found to be quite interesting being obtained as thick needles, some of which were boomerang-shaped. While examining these crystals under the microscope, it was also found that
some of them were curved and appeared with many striations nearly perpendicular to the crystal length (Scheme 2). These crystals were investigated to find out the reasons for the appearance of curvature, striations and boomerang-shapes.

Crystals of 135C246I were separated carefully into normal, curved and V-shaped categories based on their appearance. Normal crystals were used to obtain the X-ray data and the V-shaped crystals which were found to be twinned will be discussed in the next section. Surprisingly, curvature was also observed when a normal (undeformed) crystal of 135C246I or 135B246I-T was pushed from opposite sides with metal needles roughly perpendicular to their length. Shearing occurred easily along (100) planes. Depending upon the direction and amount of stress applied on these crystals they transform into various shapes and/or cleave along the planes, as shown in Figure 10. This is similar to the shearing seen in single crystals of Cu (Figure 6c). This phenomenon, although not unprecedented, is certainly unusual in organic crystals, because usually organic crystals break when subject to a mechanical shear stress and generally do not shear in this manner.

After the shear deformation, crystals became curved and developed many striations at the regions where mechanical force was applied. Striations were also developed while separating the crystals from its mother liquor and handling at the microscope. A number of striations in Figure 11 show that they correspond to the shearing movement of (100) layers within a crystal of 135C246I. The shearing direction corresponds to sliding of the (100) planes past one another. This deformation process has other parallels in the inorganic solid state and resembles the shearing of graphite [2.17a]. In contrast, when the crystal was attempted to shear or cut in other directions, the crystal broke. These directions would correspond to disrupting the layer structure—the difficulty in so doing confirms that the intralayer interactions are strong and directionally specific (synthon forming). When these crystals were subjected to a three-point bend test, they simply cleaved along the (100) planes.
Figure 10. Crystals of 135C246I sheared into different shapes by applying stress at various points. An undeformed crystal is shown in the middle. Notice the striations and slippage of planes in these crystals.

Figure 11. Shearing of crystals of 135C246I: (a) unsheared specimen elongated along [100]; (b) after shearing. Notice the striations of slip along (100); (c) broken specimen after an attempt to cut it in a direction perpendicular to the shear plane; (d) and (e) multiple shearing. The similarity to Figure 8c may be noted.
A necessary condition for shearing is the presence of a layered structure. For example, $\text{135I246M}$, $\text{135B246M}$, $\text{135B246I:135C246I}$, $\text{135B246I:135I246M}$, $\text{135C246I:135I246M}$ and $\text{135C246I:135B246M}$ (see Chapter 5 for their crystal structures) also show this layered packing and shear just as easily. Compounds without layered packing do not show shearing on the application of a mechanical stress. They either break or bend. For instance, the monoclinic polymorph of $\text{135B246I}$, with a disordered corrugated layered structure, does not show shearing on application of a mechanical stress. In fact, it simply breaks down into pieces. There is a clear relationship between the appearance of a layered structure and susceptibility to mechanical shearing of layers. Such behaviour is often encountered in the study of plasticity of inorganic crystals. Such a relationship is mediated by dislocation movements within each layer, e.g., basal slip in hexagonal inorganic crystals like Zn, Cd and Mg. This deformation process has other parallels in the inorganic solid state and resembles the shearing of graphite [2.17], which has a layered structure, and polytypism in the layered CdI$_2$ [2.8, 2.18]. In the context of X···X interactions, the significant fact obtained from these experiments is that in $\text{135C246I}$ the intralayer I···I interactions are much more important than the interlayer I···I and I···Cl interactions. To confirm the relationship between shearing and the appearance of a $\sim 4$ Å layered structure [2.19]. Similar experiments were carried out on molecular crystals of 6-chloro-2,4-dinitroaniline, $\text{1}$ and 4-nitroacetophenone, $\text{2}$, which have completely different functional groups on the aromatic ring.

**6-Chloro-2,4-dinitroaniline, $\text{1}$**

Form I of trimorphic 6-chloro-2,4-dinitroaniline, $\text{1}$ has a layered structure in the monoclinic, $P2_1/c$ space group [2.5]. The short axis of the reported monoclinic form is 7.886 Å (nearly $2 \times 4$ Å) and the layers are stacked in an antiparallel fashion at separations of 3.057 Å and 3.209 Å (Figure 12). Layers are formed via N–H···O, C–H···O, C–H···Cl and C–Cl···O interactions. In this structure, intralayer C–H···O and C–H···Cl interactions are considered to be strong since the C–H groups are unusually activated by two nitro groups. The interlayer interactions are of the van der Waals type
and are non-specific. These crystals also underwent shearing on application of a mechanical stress and became irregular (Figure 13) as expected. This example makes it clear that shearing is not restricted only to the haloaromatics discussed above and that it is a widespread phenomenon among layered structures. The mechanical behaviour of the other two forms (Form II, corrugated layered structure and Form III, 3D-interlocked hydrogen bonded structure) will be discussed in Chapter 3.

![Figure 12. 6-Chloro-2,4-dinitroaniline, 1. Layer structure to show N–H···O, C–H···O, C–H···Cl and C–Cl···O interactions.](image)

![Figure 13. Crystal of Form I (a) before and (b) after shearing. The arrows show the direction along which the shear stress was applied.](image)

4-Nitroacetophenone, 2

In the crystal structure of 4-nitroacetophenone, 2, molecules adopt a planar conformation in a 2D-layered packing (Figure 14) [2.20]. Layers are formed via C–H···O (d/Å, θ°; 2.405, 136.78; 2.599, 140.01; 2.603, 162.78) interactions. Interlayer
interactions are of the weak van der Waals space filling type. The methyl hydrogen atoms of the acetyl group emerge into the interlayer space to form weak C–H⋯O (2.758 Å, 171.34 °) interlayer interactions.

Figure 14. 4-Nitroacetophenone, 2. (a) Single planar layer (101) shows C–H⋯O interactions. (b) View down [010] shows stacking of parallel layers and a very weak interlayer C–H⋯O (2.758 Å) interaction.

Mechanical experiments on these crystals revealed that the shearing is not possible as seen in crystals of 135C2461. However, layers of these crystals cleave easily and break down into slices on application of a mechanical shear stress. Although the interlayer interactions are weak in this structure, the crystals do not show shearing which is an indication of some specificity in the interlayer interactions. It is possible that in the shearing process, sliding layers have to encounter unfavorable repulsive C(δ+)=O(δ−)...(δ−)O=C(δ+) interactions and locking of methyl groups (bumps on bumps) from molecules in the adjacent layers. Since the structure cannot afford to have these unfavourable interactions, layers would prefer to cleave rather than shear. The similar behaviour is observed in metal crystals when the shear strength is greater than the cleavage stress. In general, shear strength of a crystal will be more when the interlayer interactions are directional. Shearing of these crystals was also tried at higher temperatures, indeed up to the melting point 80 °C, but there was no evidence for shearing.
2.6 Twinning

That the non-specificity of the weak interlayer interactions is vital for shearing is further confirmed by the structure of the boomerang or V-shaped crystals of 135C246I and 135B246I-T. Crystals with these distinctive shapes were obtained for every compound for which shearing was possible. Boomerang-shaped crystals of 135B246I-T were mounted as such on a goniometer tip and X-ray data were collected (Figure 15). It was confirmed that twinning occurs at the hinge plane and that the common plane between the twins is (100) which is also the shearing layer mentioned above. A plausible twinning model is one in which two consecutive inverted layers in the normal structure are twisted by 60° and layers across the twin boundary are packed in a bumps-in-hollows fashion (Figure 16). This is preferred to a model in which the twins are mirror related because in the latter case, layers across the twin boundary would be packed in a bumps-on-bumps fashion. In general, the stacking of layers across the twin boundary is not as satisfactory as for the inverted layers in the untwinned crystal.

Figure 15. Twinning in 135B246I-T: (a) twinned crystals; (b) twinned crystal as mounted on goniometer tip, used for X-ray measurements; (c) and (d) indexing of twin faces showing common plane (100). Notice that this is the plane that contains the structure determining I₃-supramolecular synthons.
Figure 16. A schematic depiction of twinning shows that rotation by 60° achieves a boomerang shape.

Generally, bent or boomerang shaped crystals were obtained in all the structures that undergo shearing. However, in the 2:98 solid solution of 135B246M:135C246I, grown from THF, multiple twinning was observed within the same crystal (Figure 17). In addition to the usual single hinged (V-shape) crystals, double hinged (N-shape), triple hinged (W-shape) and multiple hinged ("alkyl chain type zigzag") crystals were observed. All these crystals were grown as such from solution and obtained without mechanical deformation. The fact that twinning is easy and the twin boundaries always have a local minimum in free energy [2.21] suggests that normal and twinned stacking are energetically comparable. In other words, the interlayer I···I, Br···Br and I···Br interactions are non-specific, and this is important in the context of the shearing mechanism.

Figure 17. Crystals of 135B246M:135C246I: (a) triple hinged (w-type) crystal. (b) Multiple hinged ("alkyl chain” type) crystal.
2.7 Anisotropy in Molecular Crystals

The directional nature of thermal expansion can reveal some qualitative anisotropic features of the intermolecular forces in molecular crystals. In general, any direction in which intermolecular attraction is strong should have a relatively small coefficient of thermal expansion, while weak bond directions are expected to exhibit large expansion coefficients. To confirm the anisotropy of intermolecular interactions in the 1,3,5-substituted compounds, the cell parameters of 135B246I-T and 135C246I were determined at six different temperatures between 100 K and 300 K (Figure 18). The \( a \)-axis length (short axis) increases markedly with temperature compared to the other parameters (Table 1).

![Graph showing variation of cell parameters with respect to temperature for compounds 135C246I (left) and 135B246I-T (right). Notice that the \( a \)-axis length increases markedly with temperature compared with the other parameters.](image)

However, the change in the cell parameters cannot be directly correlated to the strength of the intermolecular interactions because the expansion coefficients also mirror the relative amount of expandable “empty” space in that direction [2.22]. Thus, directions corresponding to the longest molecular axis or the shortest intermolecular contacts will exhibit minimal expansion from purely geometrical reasons. The three cell lengths in these crystals are comparable but the expandable empty space is more in the \( a \)-
direction. Even after considering all these geometrical factors, the large difference in the expansion of the \( a \)-axis cell edge gives an indication that the interlayer interactions are weaker than the intralayer ones. An analogous situation in inorganic crystals is the anisotropic thermal expansion in metals like Zn and U.

Table 1. Variable temperature cell parameters \((d/\text{Å}; \theta/°)\) of 135B246I-T and 135C246I

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135C246I

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2.8 Conclusions

To conclude, shearing of organic crystals is a common phenomenon and occurs in layered structures wherein the intralayer interactions are strong and specific, and the interlayer interactions are non-specific and weak. The intralayer interactions are directionally specific and form synthons in a planar layer, the structure of which is conserved in the normal, sheared and twinned specimens. In contrast, the interlayer
interactions are shape based and non-specific. This combination of specific intralayer interactions and non-specific interlayer interactions leads to shearing. Accordingly it may be concluded that X···X interactions (X = Cl, Br, I) are of several types and that it is sometimes difficult to characterize them using only geometrical criteria. The use of an independent technique, like observation of the mechanical behaviour of the crystal, offers a much clearer insight into their nature. The softness of the halogenated crystals is reminiscent of CdI$_2$ wherein layers of I-atoms form a close packed array and which shows similar anisotropic behavior. Whether or not these layered structures would exhibit polytypism like CdI$_2$ is still an open question but stacking faults are undoubtedly present. Mechanical experiments provide an excellent opportunity to study the nature of π···π interactions and the anisotropic behaviour of interactions in molecular crystals. From the present study it is clear that shearing is not possible in all layered molecular crystals, and that the required chemical and geometrical conditions, strength and specificity or otherwise of interlayer interactions and extent of anisotropy, if present, between interlayer and intralayer interactions for shearing are yet to be investigated for deeper understanding.

The effects of geometrical factors (available empty space) on the thermal expansion of cell parameters make it difficult to estimate the anisotropy of intermolecular interactions in most molecular crystals. But my experiments on these crystals hint that these crystals are highly anisotropic and that variable temperature X-ray data may be used as a qualitative supporting technique to confirm the same.

The mechanical response of these molecular crystals resembles in some respects that of certain types of inorganic crystals like graphite, which shows shearing. It is also well known in mechanical metallurgy that in most metals, the planes on which slip or shearing takes place are usually those with closest atomic packing, while the slip direction is always the closest-packed direction in the slip plane, which is similar to that of the layered structures discussed in this chapter. As the latter class of crystals has been investigated extensively, I conclude that there is scope for understanding the mechanical behaviour of these two different classes of crystals on a common basis.
2.9 Experimental Section

Materials: Samples of 6-chloro-2,4-dinitroaniline, 4-nitroacetophenone and all reagents and solvents employed were commercially available (Lancaster) and were used as supplied without further purification. All these compounds were characterized with NMR and IR spectra. The 1H NMR spectra were recorded on Bruker Avance at 400 MHz instrument. IR spectra were recorded on a Jasco 5300 spectrometer. All melting points were measured in Fisher-Johns melting point instrument.

Synthesis: All the mixed halogenated compounds were synthesized by either bromination or iodination of the corresponding halogenated starting materials. The general bromination and iodination procedures used to prepare these compounds are given for 135B246C and 135C246I [2.23].

Bromination: A mixture of 1,3,5-trichlorobenzene (3 mmol, 556 mg) and electrolytic Fe powder (19 mmol, 1 g) was taken in a round bottomed flask and Br₂ (0.23 mol, 6 mL) was added dropwise at 273 K after which the mixture was heated at 408-413 K for 1 h. The resulting mixture was poured into 500 mL of saturated NaHSO₃ solution, the precipitate filtered off and crystallized from THF to give 900 mg of 135B246C. IR (KBr, cm⁻¹): 1317, 1271, 623; MS (70 eV): m/z (%): 414 (M⁺), 416 (M⁺ + 2), 418 (M⁺ + 4), 420 (M⁺ + 6), 422 (M⁺ + 8), 424 (M⁺ + 10), 335, 258, 107 and 77.

Iodination: H₅IO₆ (1.66 mmol, 380 mg) was dissolved in conc. H₂SO₄ (6 mL) and crushed I₂ (5 mmol, 1.27 g) was added followed by stirring for 0.5 h. Then 1,3,5-trichlorobenzene (1 mmol, 186 mg) was added to the reaction mixture, followed by stirring for 24 h at room temperature and then for 36 h at 333 K. The reaction mixture was cooled and poured onto crushed ice. The solid was filtered and recrystallized from THF to yield 390 mg of 135C246I. IR (KBr, cm⁻¹): 1647, 1292, 559, 416; MS (70 eV): m/z (%): 558 (M⁺), 560 (M⁺ + 2), 562 (M⁺ + 4), 431, 304, 234, 179, 142, 127, 107 and 72.

1H NMR: (400 MHz, [D₆]DMSO, 25 ºC, TMS): No peaks were found in the spectrum for all the hexahalogenated compounds.
Crystallization: All the compounds were crystallized from either CCl₄, THF or 1,4-dioxane by slow evaporation at ambient temperature.

X-Ray Crystallography: Face indexing was done on a Bruker Nonius Smart Apex CCD with graphite monochromated Mo-Kα radiation. For twinned crystals reflections were sorted out using program RLAT version 3.0 and obtained the cell values for both the twinned regions. Full data collection details are discussed in Chapter 5.