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Pseudosymmetric Layers in High-*Z'* and *P*1 Structures of Organic Molecules

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Abstract

Layers having obvious approximate symmetry higher than that of the overall 3-D crystal are present in 20–25% of the *Z*'>4 and *P*1 organic structures archived in the Cambridge Structural Database (Groom *et al*., *Acta Cryst.* 2016, **B72**, 171–179). Such layers were found in 72 of *ca*. 300 organic structures having more than four crystallographically independent formula units. In roughly a third of the 72 the approximate layer symmetry is broken by offsets perpendicular to the layer normal. In another third some of the independent layers are related by a local rotation, glide, or inversion operation. In the final third there are two or more layer types that differ in packing arrangement, pattern of strong interactions (*e.g.*, H bonds), or even composition. If layers are related by simple offsets only, symmetry lowering could have taken place after crystal nucleation, perhaps as a consequence of cooling. If, however, alternating layers differ substantially in arrangement or orientation then the pattern would have had to be established at the time of nucleation. Layers of obvious approximate symmetry were also found in 136 members (22%) of a validated subset containing 615 (43%) of the 1422 (as of May 2019) organic, *P*1, $2 \leq Z' \leq 4$ structures having $R \leq 0.050$. The layers in 129 of the 136 are related by a simple shift, which is the only possibility if $Z'=2$ or if the order of the approximate layer group is four. For those 129, a modulation during crystal growth or cooling probably lowered the symmetry of the original crystal nucleus.

Contents

Conventions for the drawings: the crystallographic axes in the drawings are colored red (**a**), green (**b**), and blue (**c**). Axial labels and symmetry elements are shown in black if crystallographic and in blue if approximate. If no blue labels are shown for the layer axes those labels are the same as for the 3-D structure. Minor disorder is not shown.

3. Spreadsheets (separate files) for
   - the 23 $Z'>4$ structures of type A
   - the 49 $Z>4$ structures of types S and SR
   - the 136 $P1$, $2\le Z'\le 4$ structures

Notes on the Methodology

***Operational definition of a conventional hydrogen bond*:**

Almost all hydrogen bonds shown using the default criteria in *Mercury* were accepted; those that were not had obvious unusual features, such as a perpendicular interaction with a nitro group. In addition to the default definition N(H) ···O and N(H) ···N contacts having distances shorter than < Σ_{VDW} + 0.2 Å (*i.e.*, shorter than 3.07 or 3.10 Å) were also considered to be H bonds if the geometries looked right.

***Structures in which layers are connected by H bonds to layers of intervening solvent molecules*:**

WOPVOO ($P2_1/c$, Z'=5) Centrosymmetric layers (001) at z=0 and z=½ are related by the c glide; the layers each contain two sets of the five independent molecules. The layers are connected by H bonds through layers at z=¼ and z=¾ containing two sets each of four DMSO and two water molecules. The non-solvent layers at z=0 and z=½ differ in that one has a pseudotranslation [120]/5 while the other has pseudotranslation $[1\bar{2}0]$/5.

ZATLAJ03 ($P2_1$, Z'=8) Benzene-1,2-diaminium sulfate monohydrate plus two extra sulfuric acid molecules, which are reported to have donated one H^+ each to a water molecule. Layers (010) of the large cation and the sulfate anions are centered at y=0.174 and y=0.674. The layers are separated by the waters and the hydrogensulfate ions.

GEHWIA ($P1$, Z=Z'=2) Brucinium hydrogen L-malate pentahydrate. Ion layers (001) that have approximate $c211$ symmetry are linked by H-bonds through layers centered at z=0.36 of the ten water molecules.

***Determining layer boundaries*:**

It is very important to determine the layer limits carefully. Consider a $P1$ structure with well separated layers (001) and an approximate 2_1 axis along **a**. The layer limits for z might be 0.0 – 1.0 but might equally well be -0.5 – 0.5 or even something more general like -0.3 – 0.7. If the layer offset is significant (as it must be if the structure is seen as layered), and if the layer limits are chosen incorrectly, then the orientations of the independent molecules will be correct for the approximate 2_1 axis but the spacing along **a** will not be even (*i.e.*, the translation will be near neither 0 nor ½). In a some structures the choice that gives the best approximate symmetry may not be the choice that gives the largest layer separation.

An example is JAVKOG ($P1$, Z=Z'=2). Bilayers (001) with $0.1<z<1.1$ have good approximate symmetry $p2_111$ but the spacing along **a** is much less regular for layers with $-0.4<z<0.1$.

Another example is FIVPOR ($P1$, Z=Z'=2), which is a kryptoracemate. Layers (001) with

$0.5<z<1.5$ have quite good approximate symmetry *p*11*a* but layers with $0.0<z<1.0$ have much less good symmetry because of the spacing between molecules.***Layer axes*:**

Because most of the *P*1 structures analyzed have a cell angle within 2° of 90° and because most of the approximate layer groups require the two axes be perpendicular, the layer axes are two of the three 3-D cell axes in 76% of the 136 *P*1, $2\leq Z'\leq 4$ structures. There is no reason, however, that the layer axes need to be axes of the conventional 3-D cell. Layers with two or three non-zero indices [*e.g.*, (*hk*0)] must have at least one layer axis that is not an axis of the 3-D cell (*e.g.*, BIHVUJ). If the approximate layer group is centered and the 3-D crystal is triclinic then the rules for choosing a conventional cell guarantee that at least one of the axes of the centered layer cell will be a linear combination of the axes of the 3-D reduced triclinic cell [*e.g.*, layers (001) in TOJRAM]. Even if two of the axes of the 3-D cell lie in the layer it may be their sum and difference (*e.g.*, [110] and [$1\bar{1}0$]) that are aligned with the approximate symmetry elements (*e.g.*, FUZTIE).

Layer axes [*uvw*] were chosen to have $u>0$. This choice means that the sign of the deviation of their angle from the ideal value (usually 90°) has no meaning.

***Conformational variation*:**

The conformations of molecules related by approximate symmetry were usually very similar, but some allowance had to be made for conformational differences that could be attributed to interactions between layers. Consider ZZZVXQ0*n*, picryl bromide, in which the rotations of the three nitro groups do not conform to the overall approximate hexagonal symmetry. Interactions between layers are almost certainly very important in determining the exact rotations of those groups. Differences in the rotations of phenyl rings between molecules related by approximate symmetry are also common.

***Checking for approximate 3-D symmetry*:**

Three-dimensional pseudosymmetry is easy to find if the low-symmetry structure was obtained by taking a higher-symmetry phase through a transition during which the crystal remained single [*e.g.*, COCMIR02 ($P\bar{1}$, $Z'=8$ at 120 K) that was derived from COCMIR01 ($P\bar{1}$, $Z'=2$ at 145 K)].

Approximate symmetry relating obvious layers can, however, be difficult to identify. The method used for checking for approximate 3-D symmetry started by finding the crystallographic translation vector to an adjacent layer or to the next nearest layer that has the smallest angle with the layer normal. Often that translation vector is the third crystallographic axis but can be some more general vector [*uvw*]. The projection of that translation vector on any special axis in the layer (*e.g.*, on the layer axis $\mathbf{a}_{layer}$ if the approximate layer group is $p2_111$ or *pb*11, and on both $\mathbf{a}_{layer}$ and $\mathbf{b}_{layer}$ if the approximate layer group is, *e.g.*, *p*112, *p*11*a*, *p*4, *pab*2, or $p2_12_12$) was then calculated. If the fractional length of the projection was near 0.00 or 0.50 (or 0.33 in some special cases) then the possibility of approximate 3-D symmetry had to be investigated. Another indication of approximate symmetry in the third dimension is a very small angle between the translation vector chosen and the layer normal. Finding the corresponding higher-symmetry cell, or deciding there is none, is, however, seldom easy. Some examples follow.

KURHUC ($P1$, Z=Z'=6) There are obvious layers (010) in which there is a 2-D pattern of H bonds and there are approximate 2_1 axes along **c**; β=90.0°. There is also an approximate translation **c**/3 that affects the whole structure. The layer group would be $p2_111$ with axes $\mathbf{a}_{layer} = \mathbf{c}/3$ and $\mathbf{b}_{layer} = \mathbf{a}$ but the projection of **b** (the third axis) on **c** is 0.34, so is 1.02 on $\mathbf{a}_{layer} = \mathbf{c}/3$. The transformation $(1\ 0\ 0 \mid 0\ 0\ \tfrac{1}{3} \mid 0\ \bar{1}\ \tfrac{1}{3})$ gives a cell with angles 90.4, 92.9, and 90.0° and Z=2, which gives Z'=1 for an approximate $P2_1$ cell. The angles of the conventional $P1$ cell (69.4, 90.0, and 87.3°) give no obvious hint of the 3-D pseudosymmetry.

NULBIH ($P2_1$, Z'=6, Z=12) There are obvious layers (101) containing all six molecules; that layer has approximate symmetry $p2_1/b11$ for axes $\mathbf{a}_{layer} = \mathbf{b}$ and $\mathbf{b}_{layer} = [\bar{1}01]/3$. The transformation $(\tfrac{1}{3}\ 0\ \tfrac{1}{3} \mid 0\ 1\ 0 \mid \bar{1}\ 0\ 0)$ gives a cell with $\alpha=\gamma$=90° and Z=4, so that Z'=1 for space group $P2_1/n$. *PLATON* notices the approximate inversion center but makes no recommendation for a space-group change. With increased tolerances *PLATON* also notices approximate translations but does not recommend any change of the cell dimensions.

ILIFAK ($P1$, Z=Z'=8) There are two possible layers: (110) and (001). There are two sets of four molecules. A pseudotranslation $[1\bar{1}0]/4$ relates three of the four N-(*p*-toluenesulfonyl)-aspartic acid dimethyl ester molecules in each set and all four of the $NS(=O)_2OPh(4\text{-}Me)$ groups in each set. Layers (110) are obvious, as are the pseudotranslation and approximate 2_1 axes. The transformation $(\ 1\tfrac{1}{4}\ \ \tfrac{3}{4}\ 0 \mid \tfrac{\bar{1}}{4}\ \tfrac{1}{4}\ 0 \mid 0\ 0\ 1\ )$ gives a cell having angles 88.1, 98.7, and 91.1° and Z=4. Slices (001), which contain $[1\bar{1}0]/4$ and [530]/4, are obviously centered [molecules #1, 2, 6, 7 with centroids having $-0.1<z<0.1$; molecules #3, 4, 5, 8 with centroids having $0.4<z<0.5$]. The quite approximate twofold axes that alternate with the 2_1 axes are difficult to see because of molecular overlap, but are visible in a slice $(11\bar{1})$. The approximate space group is then $C2$ with Z'=1.

In most cases of layered structures the calculated layer offset along a special axis is in the range 0.20 – 0.30, but a value in the larger range 0.10 – 0.40 almost always indicates a significant offset. On the other hand, offset values that differ from 0.00 or 0.50 by 0.05 or less almost always indicate simple distortion of a 3-D structure. If there is 3-D pseudosymmetry the approximate symmetry relating layers is obvious if the structure is viewed from the right direction. In the case of a distorted *C*2 or *C*2/*c* cell, for example, the approximate twofold axes can be found, although perhaps not without considerable effort.

It is also useful to check the "Scanning Tables" in Part 6 of Vol. E of *International Tables* to see what exact "sectional layer groups" describe possible layers of the 3-D structure. Sometimes the approximate symmetry of a layer corresponds to a sectional layer group of the 3-D structure and sometimes it does not.

In the following structures the approximate layer symmetries correspond to a sectional layer group of the 3-D structure:

IYUWAB ($C2$, Z'=5) has two layers (100) that both have exact, but different, symmetries; the two layers are sectional layer groups of space group $C2$ with $\mathbf{a}_{layer} = \mathbf{b}$ and $\mathbf{b}_{layer} = \mathbf{c}$. The layer of molecules #1 and 2 at x=¼ has crystallographic symmetry $p2_111$, z'=2. The layer at x=0 of molecules #3, 4, and 5 has symmetry $p211$, z'=3. The packing in the two layers is very different.

JUXJIX ($P2_1/n$, Z'=6) also has two layers (010) that both have exact but different symmetry; the two layers are sectional layer groups of space group $P2_1/n$ with $\mathbf{a}_{layer} = \mathbf{a}$ and $\mathbf{b}_{layer} = \mathbf{c}$. The layer of molecules #3, 4, and 6 at y=0 has symmetry $p\bar{1}$, z'=3; the layer of molecules #1, 2, and 5 at y=¼ has symmetry $p11n$, z'=3. The packing in the two layers is very different. (Note that JUXJIX has four independent, longish NH···O bonds (> Σ_{VDW}) between the two types of layers.)

The approximate layer symmetry does not correspond to a sectional layer group in SLFNMA02, which was discussed by Bryant *et al.* (2018). The space group is $Pn2_1a$, which is $Pna2_1$ (#33) with axes **b** and **c** switched; there are layers (010). The approximate layer group symmetry is $p2_1/b11$, #17 for $\mathbf{a}_{layer}$=**c** and $\mathbf{b}_{layer}$=**a**; the 2_1 and $\bar{1}$ operations are approximate while the glide is exact. None of the sectional layer groups of $Pna2_1$, however, includes inversion.
[There is an approximate inversion center in SLFNMA02 at 0.38, y, 0.50 (y is not given because the origin of **b** is not fixed by symmetry). There is another approximate inversion center at 0.61, y+½, 0.50 because the two layers (at y = 0.07 and 0.57) are related by the 2_1 axis. The difference of 0.23 in the x coordinates of the approximate centers makes any approximate 3-D symmetry impossible.]

YAJJEA and YUKLIB are two additional examples.

Notes on the Results

***Deviation of layer-cell angle from the ideal value*:**

In most of the layered structures identified the angle between the layer axes is within 1.5° of the

ideal value. If the deviation is larger than *ca.* 2.5° there are usually noticeable deviations from the approximate symmetry. BOVDAS ($P\bar{1}$, *Z'*=4) is perhaps an example. The layers (001) at *z*=0 have quite good approximate symmetry $p2_1/b11$ (with exact $\bar{1}$s) even though the cell angle 93.0°; the distortions from that symmetry are, however, easy to identify.
(The layers at *z*=½ have exact inversion centers and an approximate **b**/2 translation. BOVDAS is another example of a structure in which adjacent layers have very different molecular arrangements.)

***Frequency of layered structures*:**
The number of unique *P*1, 2<Z'≤4 structures examined and found to be reliable was 615, of which 136 (22%) met the criteria described given in the section headed PROCEDURE.
The number of unique, reliable *Z*´>4 structures examined was just under 300, of which 72 (24%) met the same criteria.

***Types of layered structures*:**
The seven P1, Z'≤4 structures that are not of type S:

ACEZOX (*P*1, *Z'*=4; type SR) Approximate layer cell $p2_111$, *z'*=1 with layer axes **a** and **b**. Layers composed of molecules #3&4 with their approximate 2_1 axes along **a** alternate with layers of #1&2 that have approximate 2_1 axes along **b**. Cell constants *a*=10.08, *b*=10.09 Å and *α*=88.4, *β*=88.6, *γ*=90.0°. There is only one layer of each type per cell and the layers do not have approximate twofold symmetry around their normals, so the overall symmetry cannot be distorted tetragonal.

ECEHAY (*P*1, *Z'*=4; type SR) Approximate layer cell $p2_111$, *z'*=1 with layer axes **a** and **b**. Layers composed of molecules #1&2 with their approximate 2_1 axes along **a** alternate with layers of #3&4 that have approximate 2_1 axes along **b**. Cell constants *a*=7.99, *b*=8.05 Å and *α*=96.6, *β*=96.4, *γ*=90.0°. There is only one layer of each type per cell and the layers do not have approximate twofold symmetry around their normals, so the overall symmetry cannot be distorted tetragonal.

IFAFUS (*P*1, *Z'*=3; type A) Layers (001) at *z*=0.35 of #1&3 have good layer symmetry $p2_111$ with axes $\mathbf{a}_{layer}$=**b** and $\mathbf{b}_{layer}$=**a.** The layer (001) at *z*=0.85 of molecule #2 has translational symmetry only (group *p*1). The orientation of #2 is unrelated to the orientations of #1&3.

WAZSAT (*P*1, *Z'*=4; type A) Approximate layer cell *p*112, *z'*=1 with layer axes **a** and **b**. Rigid, V-shaped molecules have good local twofold axes. Layers composed of molecules #1&2 with their approximate local twofold axes along **b** alternate with layers of #3&4 that have approximate twofold axes along **a** (*γ*=105.7°). The approximate symmetry is more exact for the layer of #3&4 than for the layer of #1&2, and the packing differs between the two layers (a=8.82, b=11.46 Å).

XURWEO ($P1$, Z'=3; type A) Layers (001) at z=-0.04 of #1&2 have good approximate layer symmetry $c211$ with axes **a** and [120] (angle 88.3°). The layer (001) at z=0.45 of #3 has translational symmetry only (group $p1$). The orientation of molecule #3 is unrelated to the orientations of #1&2.

For the remaining two examples charge balance requires that the alternating layers occur in pairs.

HUZDOV ($P1$, Z'=4; type A) $[(n\text{-Bu})_4N^+]$(2,6-dihydroxybenzoate) plus an extra molecule of 2,6-dihydroxybenzoic acid. The cations are in layers (001) at z=0.25 and 0.74 that have approximate symmetry $p\bar{4}$ (a=13.98. b=14.05 Å; γ=89.9°) and axes [110]/2 and $[1\bar{1}0]/2$ (angle 90.3°). The cations are located on a $\bar{4}$ site; the two layers are related by approximate glides with the mirror perpendicular to **c***. The anions and neutral molecules form H-bonded tetramers in layers at z=-0.00 and 0.49; these two layers have approximate symmetry $p\bar{1}$ and are offset.

TOJRAM ($P1$, Z'=2; type A) A $C_7H_8NO_2^+$, $C_2F_6NO_4S_2^-$ salt. An obvious layer (001) at z=0.63 contains both cations and one anion; the layer symmetry is approximately $c211$ with axes **b** and $[2\bar{1}0]$ (angle 92.7°) with the one anion lying on the approximate twofold axis. The second anion forms layers at z=0.14 that have translational symmetry only (group $p1$).

Other information re the P1, 2≤Z'≤4 structures:
The numbers of structures having Z'= 2, 3, and 4 are 108, 2, and 26.

Notes on Groups of Structures

Group S structures (layers stacked by translation with offsets)

If there is a layer of approximate symmetry in a $P1$ structure then the layer must have at least two independent molecules unless the molecule would be located on a special position if the layer symmetry were exact. Only three $P1$ structures were found in which molecules lie on such a position. In all the molecules would lie on twofold axes.

QUBPIN ($P1$, Z'=2) Layers (012), axes **a**, $[02\bar{1}]$; approximate layer group $pba2$ (#25), z'=½
UJADOZ ($P1$, Z'=2) Layers (010), axes **c**, **a**; approximate layer group $p2_122$ (#20), z'=½
DOVXIW ($P1$, Z'=4) Layers (100), axes **c**, **b**; approximate layer group $p2_122$ (#20), z'=2=4(½)
In all three of those structures there is only one layer type.

The 22 $P1$, Z'=4, type S structures could have two different but very similar layers composed of two independent molecules each but no such structure was found. In six of the 22 the multiplicity of the general position of the approximate layer group is four. In 11 there are two independent molecules in the approximate layer group, and in five there is an approximate translation that decreases the size of the approximate layer cell.

Only two *P*1, *Z'*=3 structures were found; both have two different layers and so are of type A.

If two or more layers in a unit cell are related by inversion or a 2_1 screw axis parallel to the layer normal then the layer axes in the two layers are parallel but the directions of the axes are reversed, which matters if at least one is polar. If neither of the layer axes is polar then inversion or a parallel 2_1 axis is similar to a translation unless the two sides of the layer are very different. If two layers are related by a 2_1 axis perpendicular to the layer normal then usually one of the layer axes has the same orientation in the two layers and the other axis does not.

Of the *Z'*>4 structures 24 are composed of layers that can be superimposed by translation. (Two more have been classified as S/SR but have been counted with the SR group.) Of those 24 five have one layer per cell so that the layers must be related by translation; in all five the offsets between adjacent layers show there is no approximate 3-D symmetry.

Four of the 24 have two layers per cell that are related by inversion or by a 2_1 axis; two more (RIKNOO and ZZZZCA03) have layers that include exact inversion centers and so have one layer per cell with adjacent layers related by inversion. In all six it can be seen easily that the symmetry relating the layers is incompatible with the approximate symmetry of the layer.

One structure (QARNAA; *P*1, *Z'*=6) has three independent layers. Since the approximate layer symmetry is at least *p*6, the **b**/3 offset between adjacent layers means that there cannot be any approximate 3-D symmetry. (Rhombohedral centering is not possible in a hexagonal group.)

The remaining 12 of the 24 all have more layers than independent layers; *i.e.*, some of the layers are related by crystallographic symmetry. In all 12 it is clear that the approximate layer symmetry cannot extend to the third dimension. There is no polar axis in the layer in any of the 12.

Group SR structures (layers stacked by a combination of reorientation and offsets)

LADQAL (*P*4_1; 4 layers), MAJSOG (*Cc*; 2 layers) and WOPVOO (*P*2_1/*c*; 2 layers) have only one layer type with the different layers related by crystallographic symmetry. The structures all have approximate translations that are local to the layers (*e.g.*, [120]/5 and [$1\bar{2}0$]/5 in WOPVOO) so that there is approximate layer symmetry that does not extend to the third dimension.

QQQBVP02 ($P\bar{1}$, 4 layers) is similar but the 90° rotation between adjacent layers is only approximate. In RUKTOI ($P1$; 2 layers) the angle between the two independent layers, each of which has approximate symmetry $c211$) is *ca.* 70° and the two local approximate translations are [201]/3 and [20$\bar{1}$]/3.

Two $P1$ structures (ACEZOX and ECEHAY) have adjacent $p2_111$ and $p12_11$ layers; the approximate screw axes are along **a** in one layer and along **b** in the next. Two Z'>4 structures, MUMHAE and UMAHAT, are similar.

ACEZOX	($P1$, Z'=4) 2 layers (001); a, b = 10.085, 10.089Å, γ = 90.0°; approximate layer groups $p2_111$, $p12_11$, z'= 1 alternate
ECEHAY	($P1$, Z'=4) 2 layers (001); a, b = 7.99, 8.05 Å, γ = 90.0°; approximate layer groups $p2_111$, $p12_11$, z'= 1 alternate
MUMHAE	($P\bar{1}$, Z'=8) 2 layers (001); a, b = 15.97, 16.49 Å, γ = 89.1°; approximate layer groups $p2_1/b11$, $p12_1/a1$, z'= 1 alternate
UMAHAT	($P1$, Z'=8) 4 layers (001); a, b = 9.18, 9.22 Å, γ = 90.0°; approximate layer groups $p2_111$, $p12_11$, z'= 1 alternate; (UMAHAT is a distorted $P2_1$ structure that would have two independent layers.)

Approximate tetragonal symmetry in the first three is impossible because there are only two layers and the layers do not have a twofold axis parallel to the layer normal (as would be required for a group with a 4_2 axis). Approximate tetragonal symmetry in the last is impossible because the position for the 4_1 axis relating layers n and n+1 varies with n.

In HASYUX ($P1$, Z'=6) the layer orientations are related by approximate threefold rotations.

FADQAF. GIPLID, and the four Z'>4 polymorphs of picryl bromide (ZZZVXQ02/03/05/06) have layers with orientations related by approximate 180° rotations around the direction of the stacking axis. COVBEV also has two layer orientations related by a *ca.* 180° rotation but there are two adjacent layers of one type and three of the other.

XAXTUL [4,6-dichloro-2-(methylthio)pyrimidine; $P\bar{1}$, Z'=6] has four layers (100) of approximate symmetry $p\bar{6}$. (b, c = 14.13, 14.13 Å, α = 120.0°). Along **a** (β, γ = 95.9, 92.8°) there are two columns of planar molecules (#5, 1, 3, 6, 5^t and #4, 2, 2^i, 4^i, 4^t). Molecules adjacent in a column are rotated around **a*** by *ca.* 60, 60, 180, and 60° and are somewhat offset.

DATTAV ($P2_1/n$, Z'=6) and QUQQUO ($P\bar{1}$, Z'=8) are both technically SR structures because adjacent layers are related by inversion or 2_1 axes perpendicular to the layer normal. In QUQQUO the approximate layer symmetry is $pba2$ so that the only polar direction is the layer normal, along which the molecule is basically globular. In DATTAV (approximate layer symmetry $pb2_1m$, with $\mathbf{b}_{layer}$=$\mathbf{c}$) the difference between the two directions of the polar axis $\mathbf{b}_{layer}$ is minor.

Group A structures (alternating layers differ)

Different composition, etc.

CIFGEE (*Z*'=5; one included water molecule in one of the two layers)
WIYSAZ (*Z*'=6=5+1; one included enantiomer in one of the two layers)

HUZDOV (*P*1, *Z*'=4; Bu_4N^+ salt; cations and anions are in different layers)
TOJRAM (*P*1, *Z*'=2; 1:1 salt; one of the two anions is in a layer by itself)

Different H-bonding patterns, etc.

IYUWAB (*Z*'=5)
KIWVES (*Z*'=5)
YAJJEA (*Z*'=5)
YUKLIB (*Z*'=5)
AGAXIZ (*Z*'=6)
UYOPAA (*Z*'=6)

Different packing patterns (usually with different approximate symmetries)

IFAFUS (*P*1, *Z*'=3)
WAZSAT (*P*1, *Z*'=4)
XURWEO (*P*1, *Z*'=3)
LIRXIU (*Z*'=5)
MOQJAE (*Z*'=5)
COJJER (*Z*'=6)
IJUDIC (*Z*'=6)
JUXJIX (*Z*'=6)
KITQIN (*Z*'=6)
OTOLIC04 (*Z*'=6)
PIPQUA (*Z*'=6)
QUJSAP (*Z*'=6)
QUYNUU (*Z*'=6)
SEBZUV (*Z*'=6)

OKOXIW (*Z*’=8)
GENLAN (*Z*’=12)

Different approximate symmetry
HAXLAV (*Z*’=6)
LEXVEP01 (*Z*’=6)

One-molecule layer separates multimolecule layers (as might solvent molecules)
IFAFUS (*Z’*=3)
XURWEO (*Z*’=3)
LIRXIU (*Z*’=5)
MOQJAE (*Z*’=5)
COJJER (*Z*’=6)

Some approximate layer groups are especially common:

The Z'>4 S and SR structures that have layers of approximate orthorhombic, tetragonal, trigonal, and hexagonal symmetry:

LADQAL ($P4_1$, $Z'=6$)	Approximate layer symmetry $p2_12_12$ (#21) or $pba2$ (#25), $z'=\frac{1}{2}$
RAKBUC ($P1$, $Z'=8$)	Approximate layer symmetry $p2_12_12$ (#21) , $z'=1$
LUMYAT (Pa, $Z'=8$)	Approximate layer symmetry $pba2$ (#25), $z'=1$
QUQQUO ($P\bar{1}$, $Z'=8$)	Approximate layer symmetry $pba2$ (#25), $z'=1$
UHIPAD ($P2_1$, $Z'=6$)	Approximate layer symmetry $p2_12_12$ (#21) , $z'=1$
DATTAV ($P2_1/n$, $Z'=6$)	Approximate layer symmetry $pb2_1m$ (#29), $z'=3$
SABPOB ($P2_12_12_1$, $Z'=7$)	Approximate layer symmetry $pb2_1m$ (#29), $z'=1$
ACOMOW ($P\bar{1}$, $Z'=12$)	Approximate layer symmetry $pbam$ (#44), $z'=1$
RIKNOO ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $pbam$ (#44), $z'=3$
TCLOBQ01 ($P2_1/n$, $Z'=7$)	Approximate layer symmetry $pbam$ (#44), $z'=1$
YEZDEN ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $pbam$ (#44) , $z'=1$
OKEKEV (Cc, $Z'=6$)	Approximate layer symmetry $cmmm$ (#47) , $z'=1$

CICTIT ($P1$, $Z'=8$)	Approximate layer symmetry $p4$ (#49), $z'=\frac{1}{2}$
PAVLAB (Cc, $Z'=8$)	Approximate layer symmetry $p\bar{4}$ (#50), $z'=1$
POVYEG ($P\bar{1}$, $Z'=8$)	Approximate layer symmetry $p\bar{4}b2$ (#60), $z'=1$

KOFTEG ($P3_2$, $Z'=6$)	Approximate layer symmetry $p3$ (#65), $z'=1$

QARNAA ($P1$, $Z'=6$)	Approximate layer symmetry $p6$ (#73), $z'=\frac{1}{3}$
FITQAA ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
XAXTUL ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
ZZZVXQ02 ($P3_1$, $Z'=12$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
ZZZVXQ03 ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
ZZZVXQ05 ($P\bar{1}$, $Z'=12$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
ZZZVXQ06 ($P1$, $Z'=18$)	Approximate layer symmetry $p\bar{6}$ (#74), $z'=1$
CEGBEW ($P\bar{1}$, $Z'=6$)	Approximate layer symmetry $p6/m$ (#75), $z'=1$
CEGBAS ($P6_1$, $Z'=6$)	Approximate layer symmetry $p6/m$ (#75), $z'=1$

The P1 2≤Z’≤4 S and SR structures that have layers of approximate orthorhombic symmetry:

BIVLIC ($P1$, Z'=4)	Approximate layer symmetry $p222$ (#19), z'=1
DOVXIW ($P1$, Z'=4)	Approximate layer symmetry $p2_122$ (#20), z'=2(½)=1
UJADOZ ($P1$, Z'=2)	Approximate layer symmetry $p2_122$ (#20), z'=½
BIHVUJ ($P1$, Z'=4)	Approximate layer symmetry $p2_12_12$ (#21), z'=1
QUBPIN ($P1$, Z'=2)	Approximate layer symmetry $pba2$ (#25), z'=½
VEHDEU ($P1$, Z'=4)	Approximate layer symmetry $pb2_1a$ (#33), z'=1
IGARIT ($P1$, Z'=4)	Approximate layer symmetry $pb2n$ (#34), z'=1

Group A structure that also has a modulation

COJJER ($P2_1$, Z'=6) Layers (001) of crystallographic symmetry $p2_111$ (a_{layer}=b, b_{layer}=a) and of approximate symmetry $p2_12_12$ have very different packing arrangements . The B layers include twice as many molecules as the A layers. There is also an approximate c/2 translation that describes the whole structure; the sequence of the layers is then A1, B, A2, A1, B^i, A1, ⋯.

Notes on the Discussion

***Some layered structures in which a phase change from a lower-Z’ structure to a higher-Z’ structure occurs with cooling*:**

COCMIR01 is $P\bar{1}$, Z'=2, Z=4 at 145 K but COCMIR02 $P\bar{1}$, Z'=8, Z=16 at 120 K

TETBUS03 is $P2_1/c$; Z'=1, Z=4 at RT but TETBUS02 is $C2$, Z'=8, Z=32 at 145 K.

(TETBUS03 is not listed in the spreadsheet because of when it was archived in the CSD.)

ZATLAJ01 is $P2_1$, Z'=4, Z=8 at 130 K but ZATLAJ03 is $P2_1$, Z'=8, Z=16 at 120 K

Additional discussion of YIQGIP

The 1:1 structure of *rac*-1,2-cyclohexanediol (CHD) and triphenylphosphine oxide (TPPO) was studied at 90 K and room temperature for crystals grown from acetone, ethanol, and toluene. The TPPO layers are ordered; the degree of R/S disorder in the CHD layers depends on the solvent from which the crystal was grown. The occupancy factors for the two independent molecules in the three $P\bar{1}$ structures determined at room temperature were:

0.86:0.14 and 0.92:0.08 for the crystal grown from acetone
0.78:0.22 and 0.86:0.14 for the crystal grown from ethanol

0.72:0.28 and 0.82:0.18 for the crystal grown from toluene

The occupancy factors at 90 K were similar; cooling did not affect the disorder significantly.

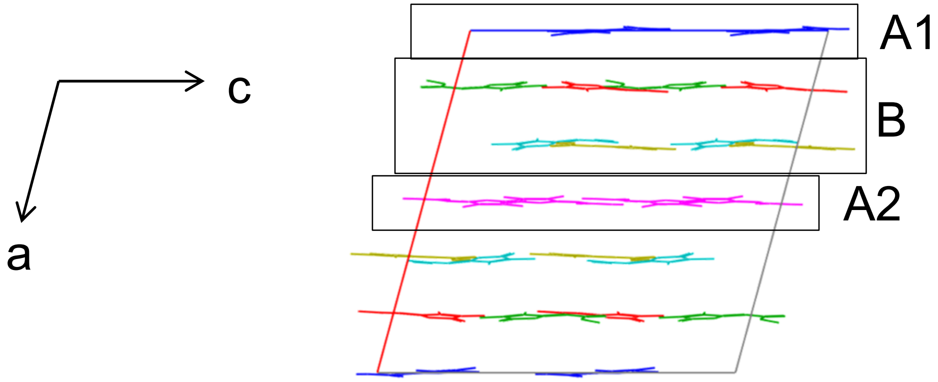
The structures could also be refined in *C*2/*c* with *Z'*=1 and a nearly 0.50:0.50 CHD disorder; the deviations for *C*2/*c* symmetry were, however, obvious. The cells are related by the transformation matrix $\mathbf{a}_{monoclinic}$ = (102/100/010) $\mathbf{a}_{triclinic}$; layers (001) in $P\bar{1}$ become (200) in *C*2/*c*. In the $P\bar{1}$ structure the (ordered) TPPO layers have approximate symmetry $p2_1/b11$ (#17) with *z'*=1 and exact inversion centers; in the *C*2/*c* structure the $p2_1/b11$ layer symmetry ($\mathbf{a}_{layer}$=**b** and $\mathbf{b}_{layer}$=**c**) is crystallographic.

In the $P\bar{1}$ structure the approximate symmetry of a CHD layer is *p*112/*b* (#7; standard setting *p*112/*a*), but in *C*2/*c* the crystallographic symmetry of the CHD layer is *p*2/*b*11 (#16), both with *z'*=1 (see drawing on pg. 150 of the ESI). The disordered CHD of the *C*2/*c* structure has approximate symmetry *pbmb* (#38, standard setting *pmaa*). That group is a supergroup of both *p*2/*b*11 and *p*112/*b.*

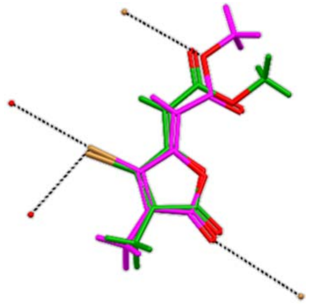
Layer groups $p2_1/b11$ (#17) and *p*2/*b*11 (#16) are both sectional layer groups of *C*2/*c* but *p*112/*b* (#7) is not. Arguments were made in the paper that individual CHD layers are at least mostly ordered, in which case the *p*112/*b* description is the better choice.

Projection along **b**

AGIXIZ
($P2_1/c$, Z'=6)



Br…O contacts are marked if the distance is shorter than ΣVDW - 0.2 Å; the interacting O atoms are different in the two layer types

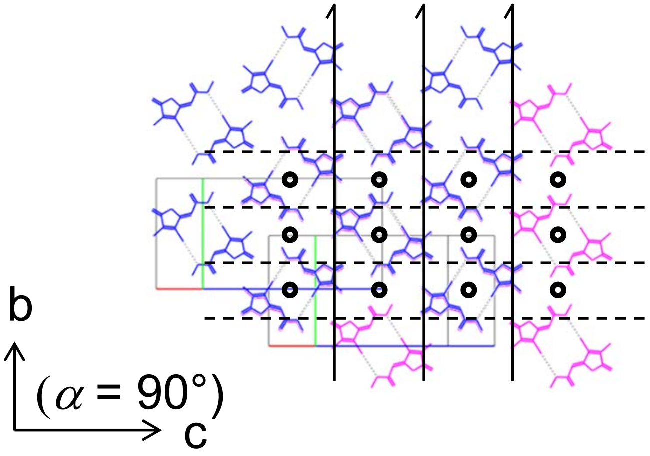


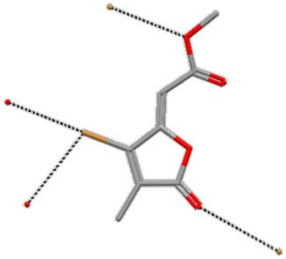
Layers (100): Overlay of A1,A2; B

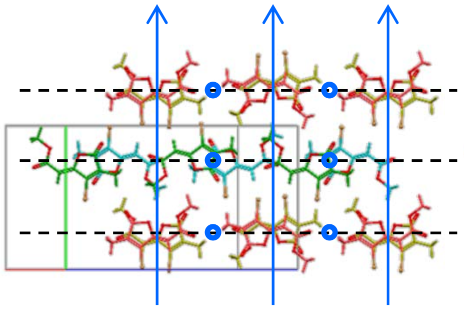
A1, A2 are also related by the approximate twofold of layer B

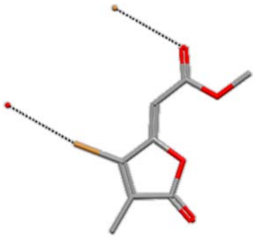
$p12_1/c1$ (#17), z'=1

$p12/c1$ (#16), z'=2



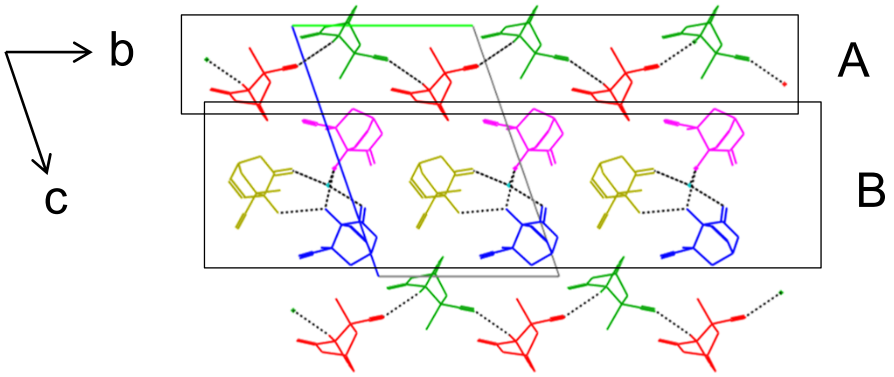






Projection along **a**

CIFGEE
($P1$, Z'=5)

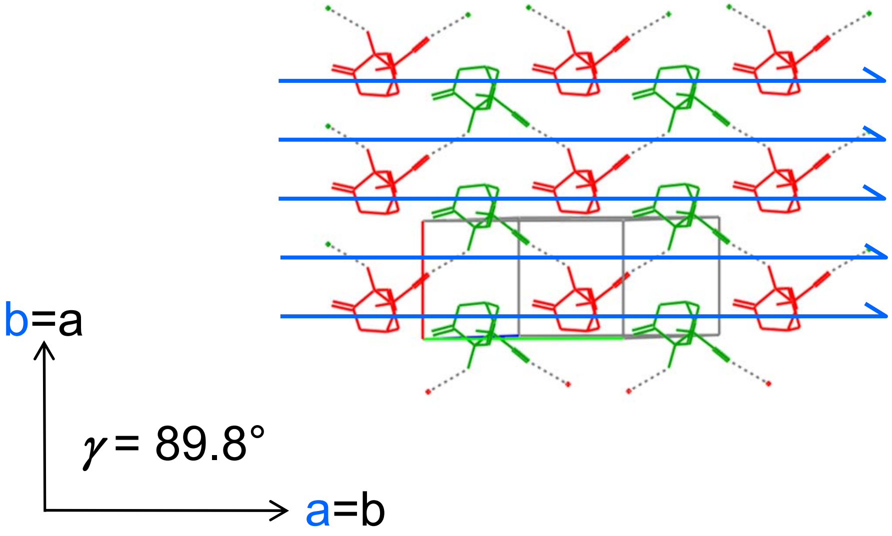


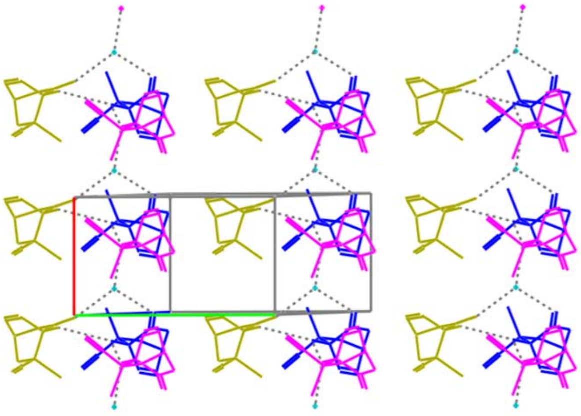
Layer B contains the one included water molecule

Layers (001) A and B

$p2_111$ (#9), z'=1

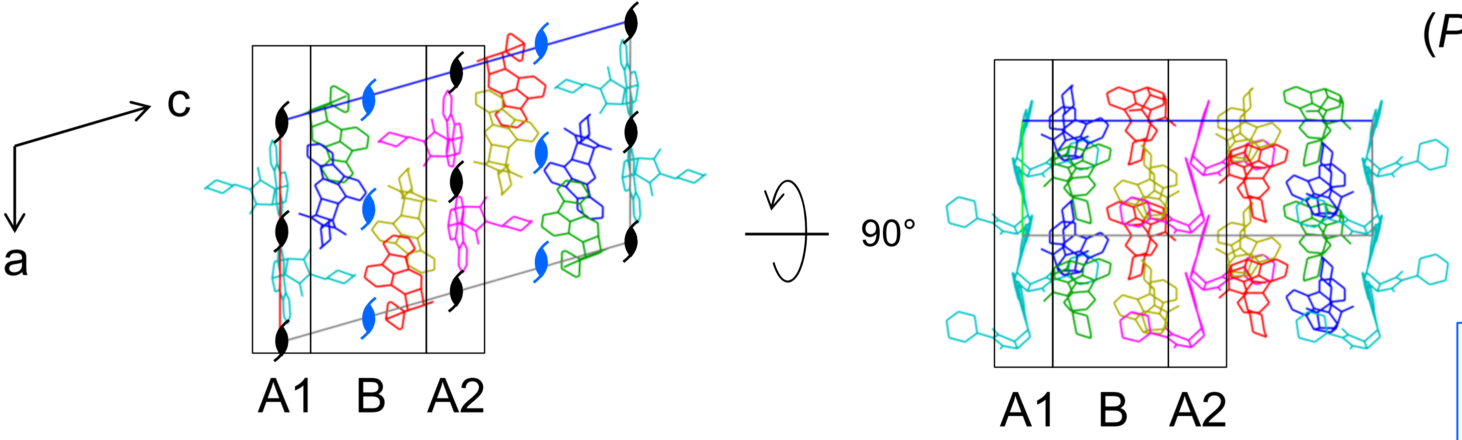
$p1$ (#1), z'=3





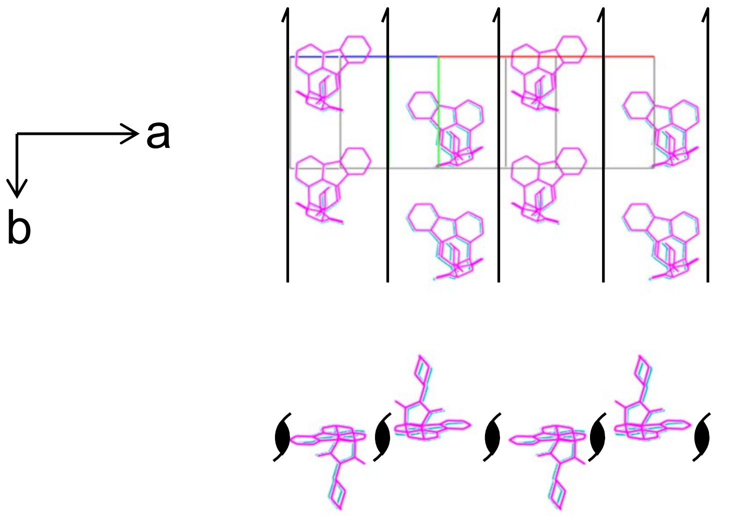
Projections along **b** and **a**

COJJER
($P2_1$, Z'=6)

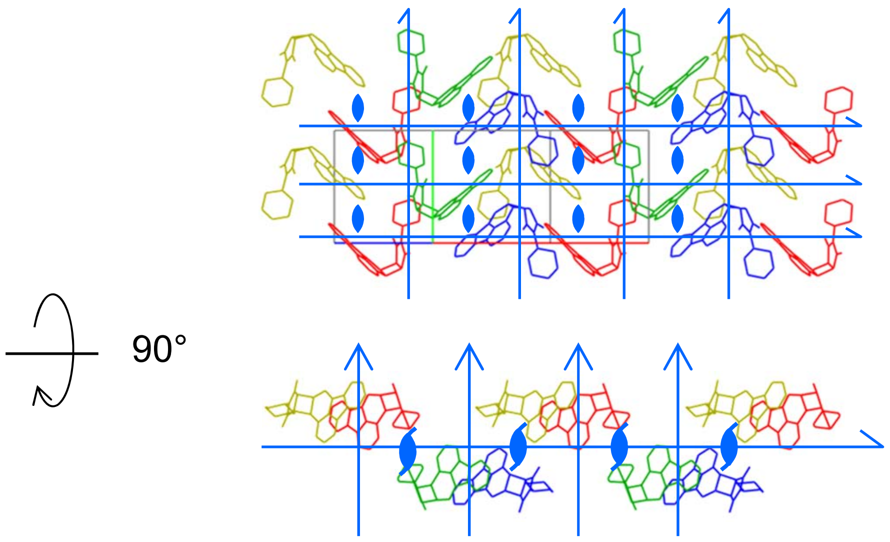


pseudo
translation
c/2

Layers (001): Overlay of A1, A2; B



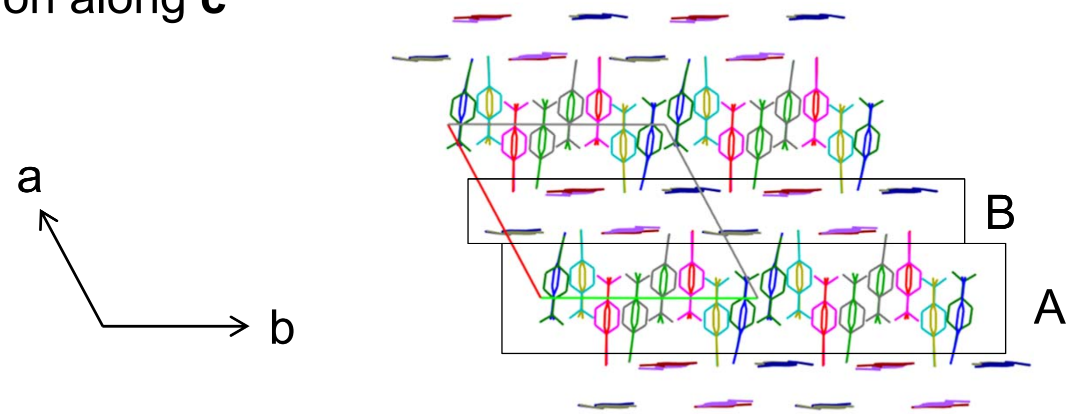
$p12_11$ (#9), z'=1



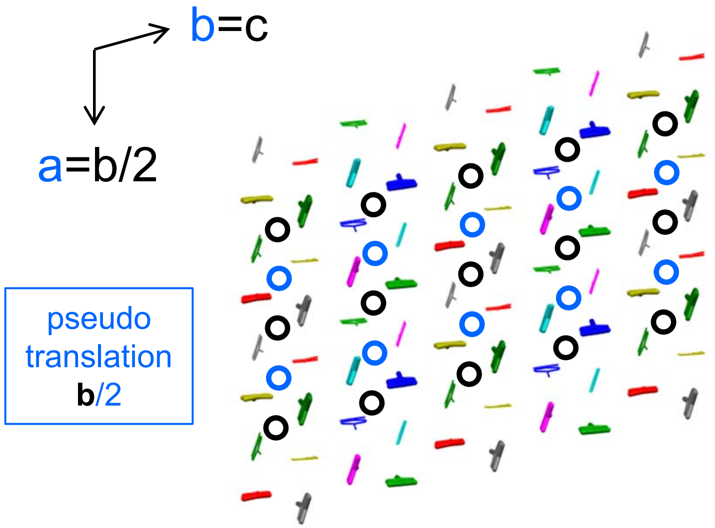
$p2_12_12$ (#21), z'=1

Projection along **c**

GENLAN
($P\bar{1}$, Z'=12)

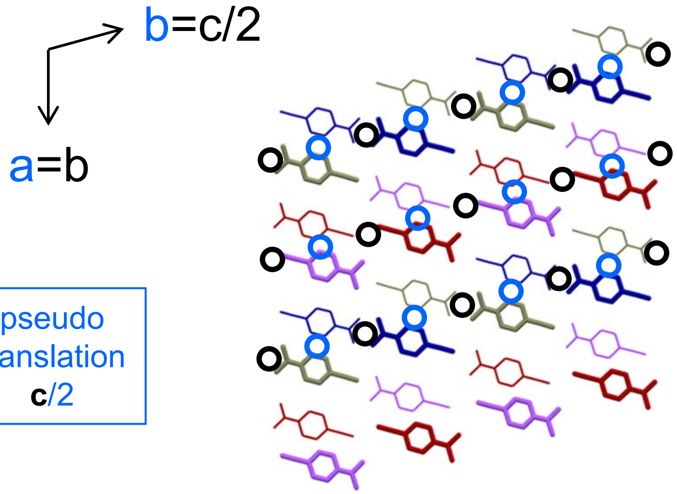


Layers (100) A and B



pseudo
translation
b/2

$p\bar{1}$ (#2), z'=4

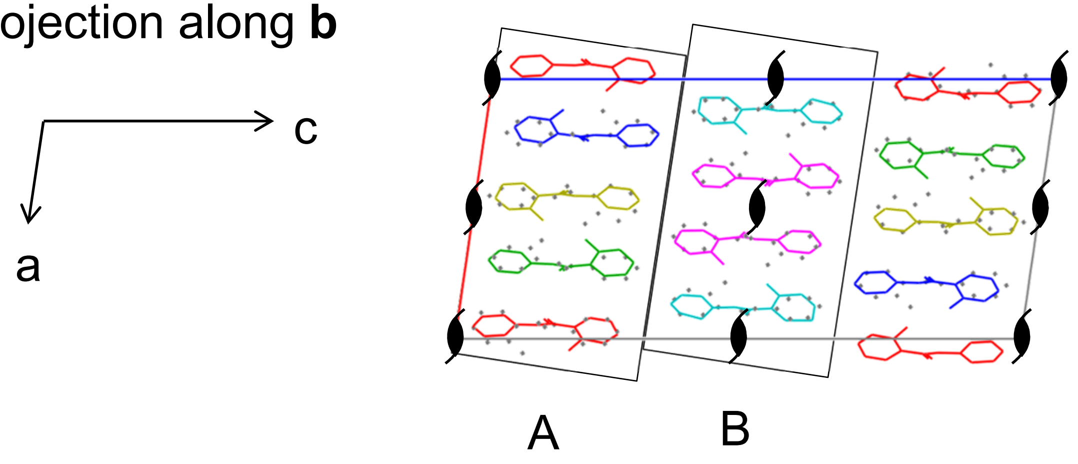


pseudo
translation
c/2

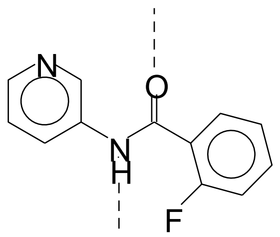
(the molecules drawn with thicker lines are at $x < 0.5$)

$p\bar{1}$ (#2), z'=2

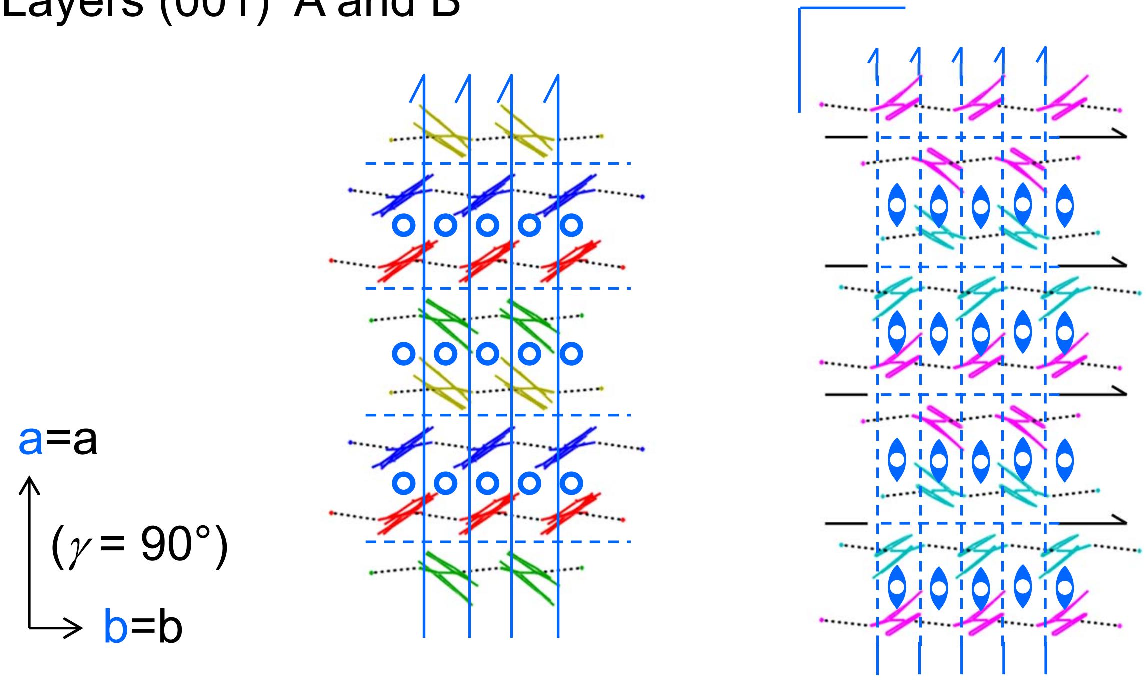
Projection along **b**



HAXLAV
($P2_1$, Z'=6)

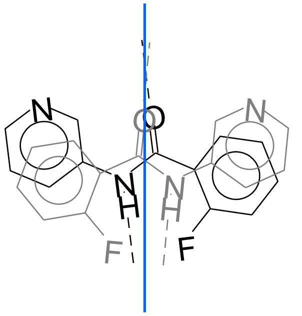


Layers (001) A and B



$p2_1/b11$ (#17), z'=1 **$pbam$ (#44), z'=1**

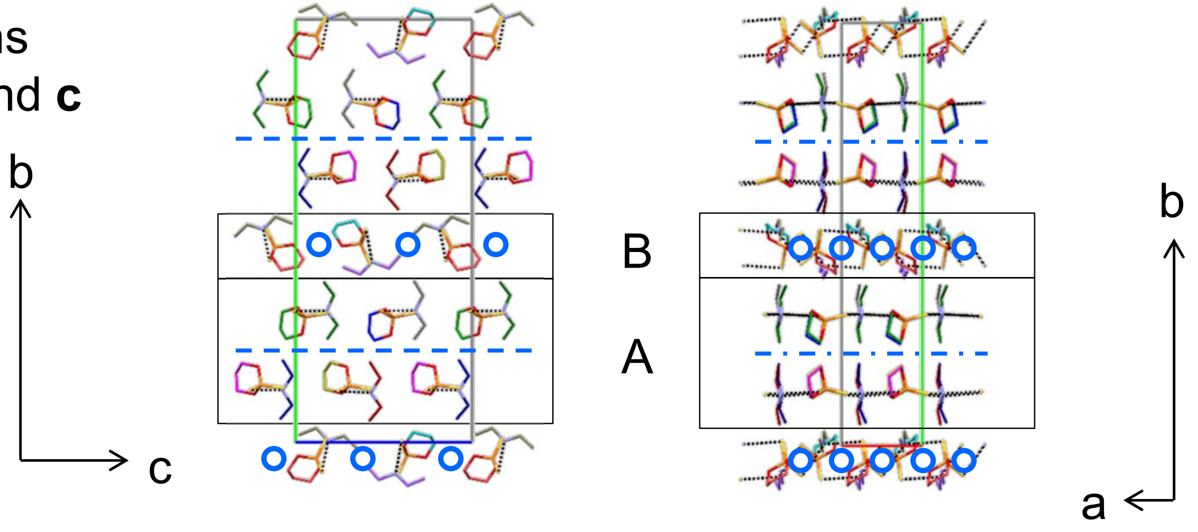
Layer B at z=1/2 has 1:1 disorder, which effectively adds a mirror within the layer



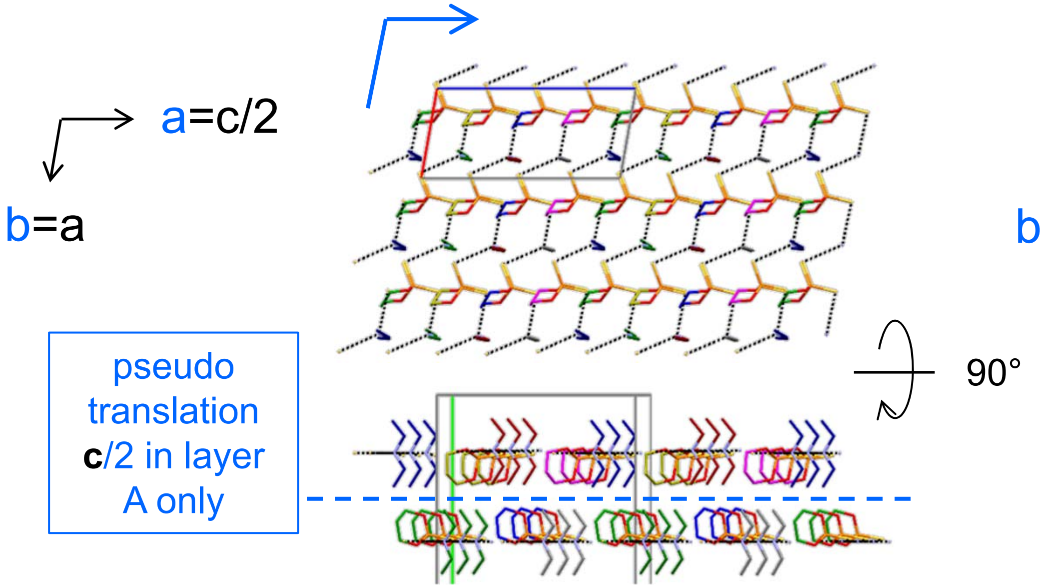
(Layer at z *ca* 1/6 has only 15% disorder)

Projections along **a** and **c**

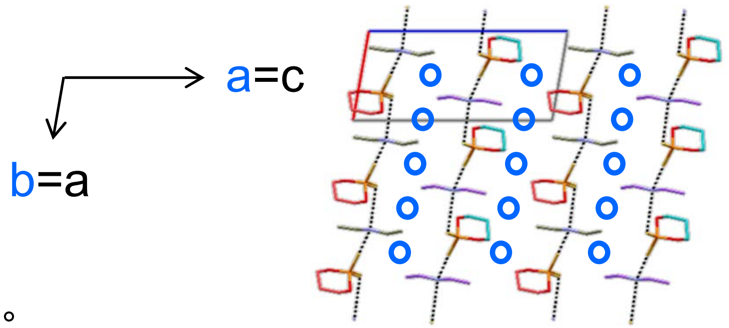
IJUDIC ($P2_1$, Z'=6)



Layers (010) A and B



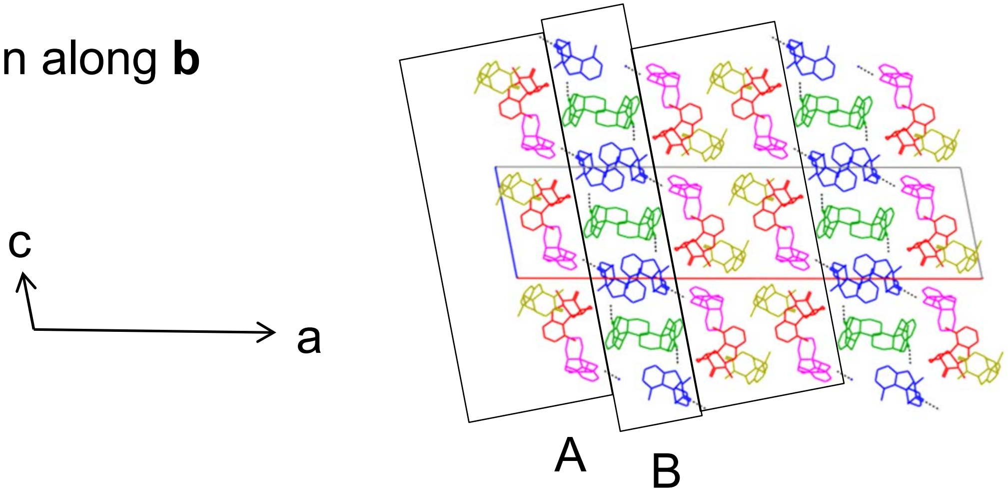
pseudo translation **c**/2 in layer A only



***p*11*a* (#5), z'=1** (for **a**=**c**/2)

***p*$\bar{1}$ (#2), *z'*=1**

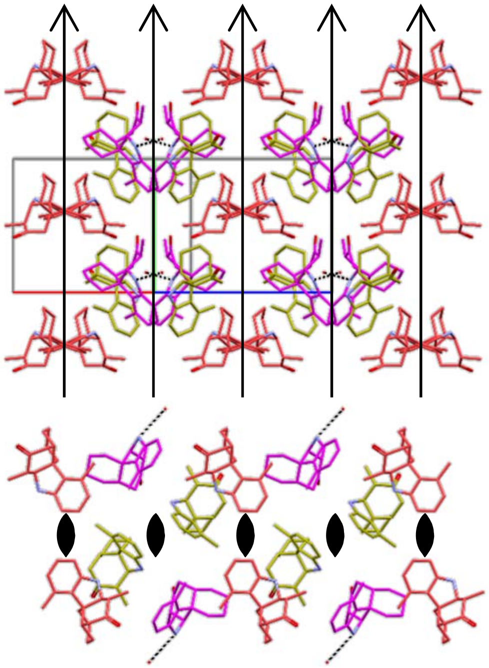
Projection along **b**



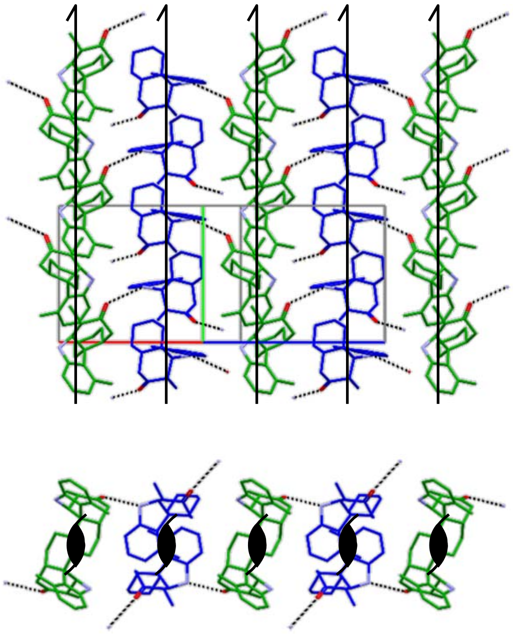
IYUWAB
($C2$, $Z'=5$)

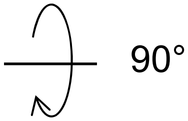
Layers (100): A and B

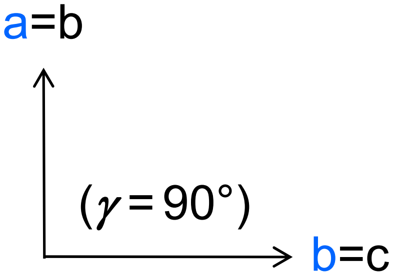
***p*211 (#8),**
***z'*=3**



***p*$2_1$11 (#9),**
***z'*=2**

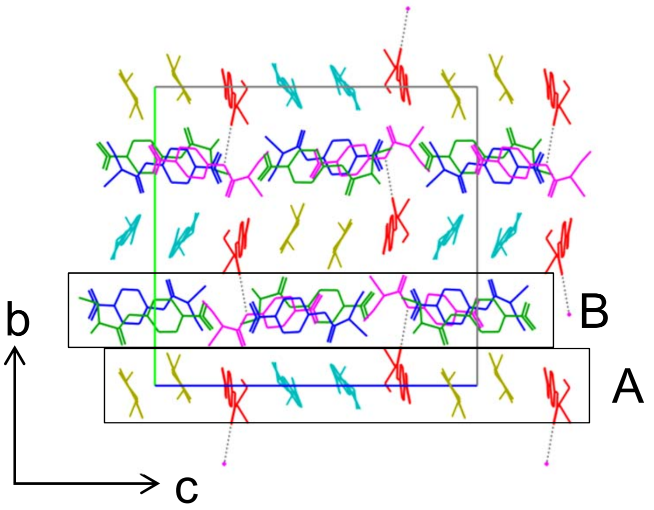


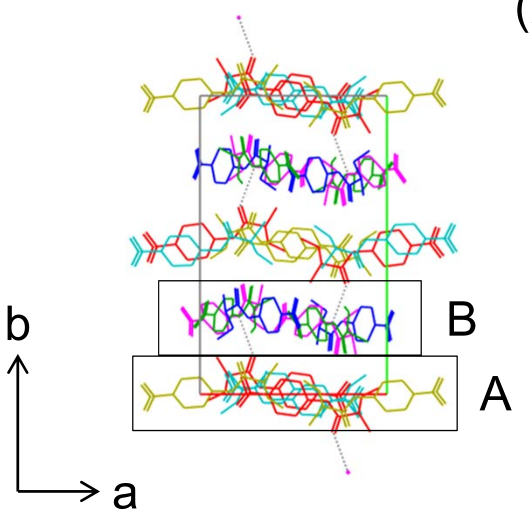




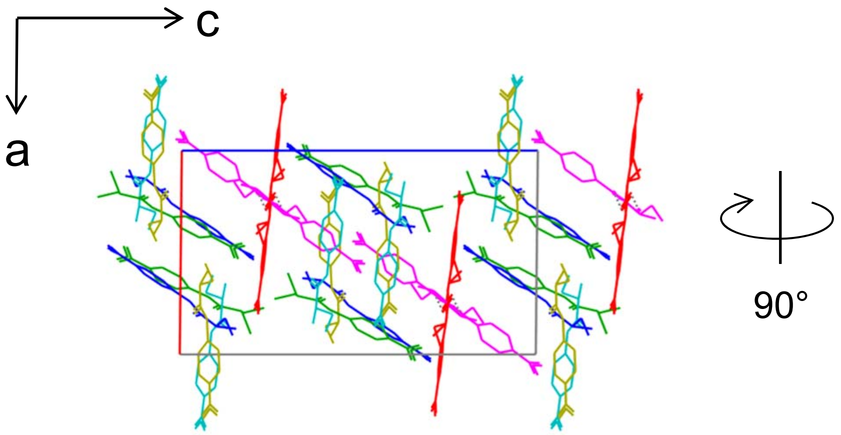
Projections along **a** and **c**

JUXJIX
($P2_1/n$, Z'=6)

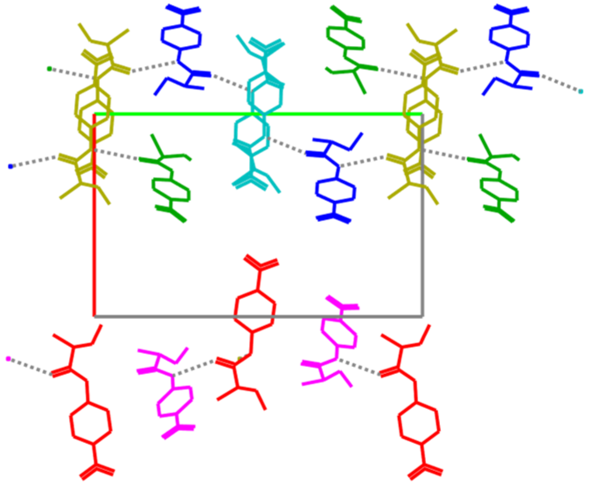




Projection along **b**



The unique part of the structure

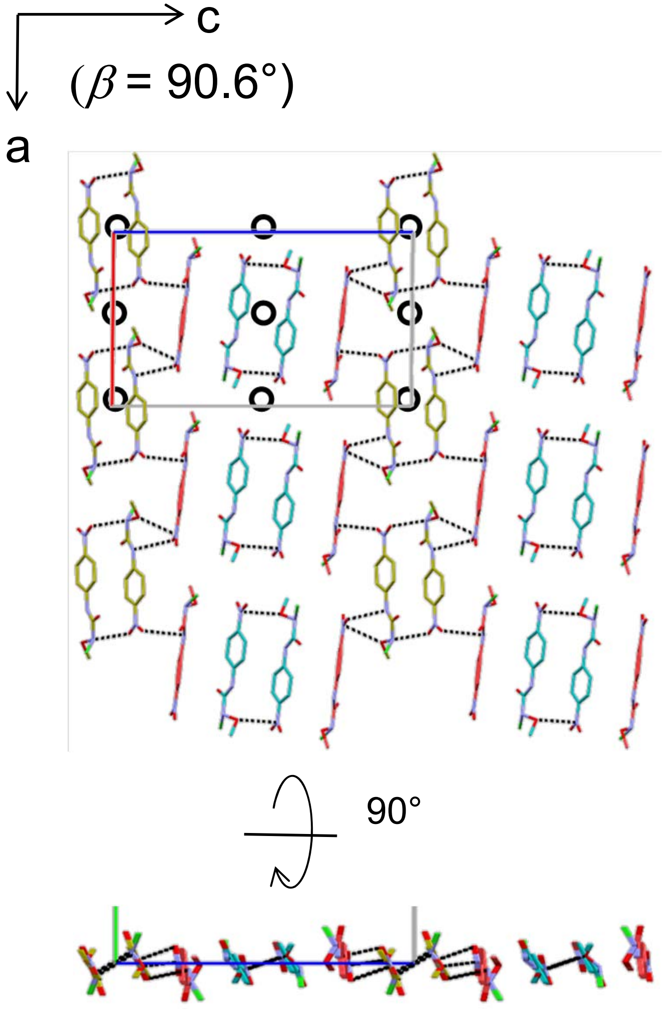


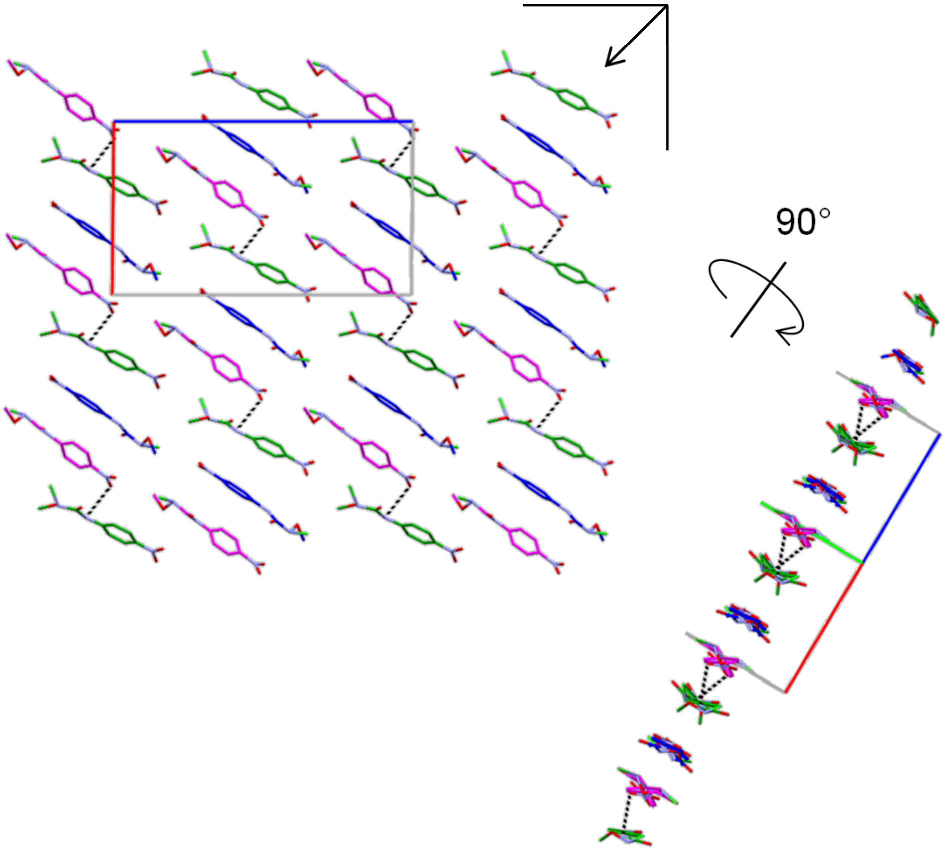
In this one drawing NH…O=C contacts are marked if the distance is shorter than ΣVDW + 0.2 Å

(see also next page)

Layers (010) A and B

JUXJIX,
con't
($P2_1/n$, Z'=6)

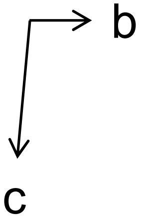


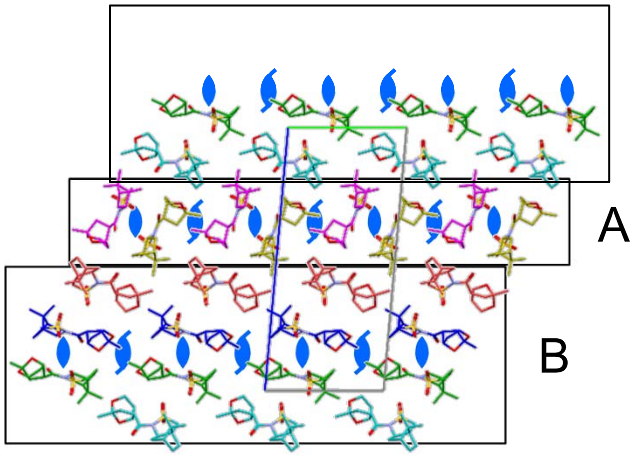


$p\bar{1}$ (#2), z'=3

$p1n1$ (#5), z'=3

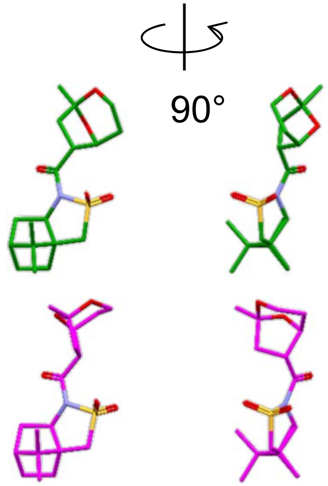
Projection along **a**





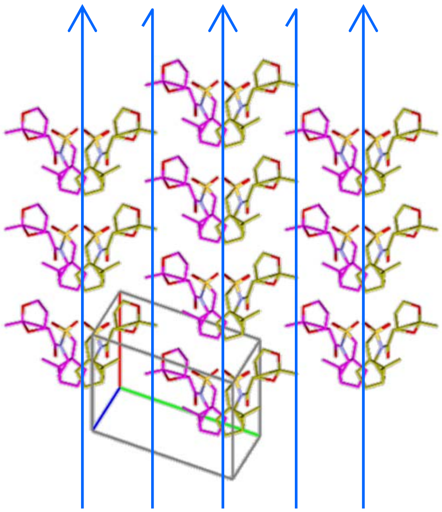
KITQIN
($P1$, Z'=6)

the conformations
in the two layer
types differ

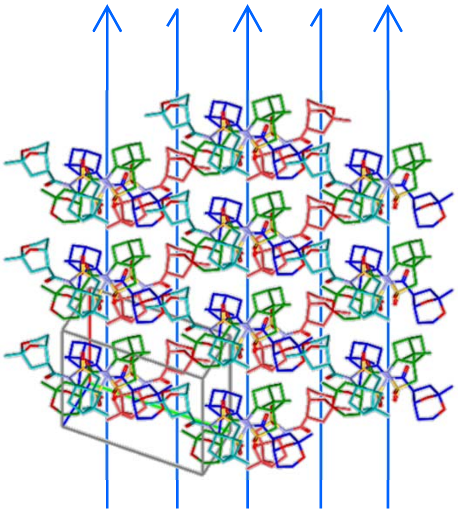


Layers (001) A and B

$c211$ (#10), z'=1

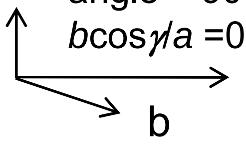


$c211$ (#10), z'=2



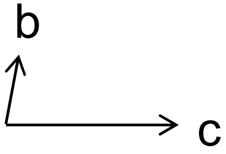
(angle of **a** with
c is 97.8°)

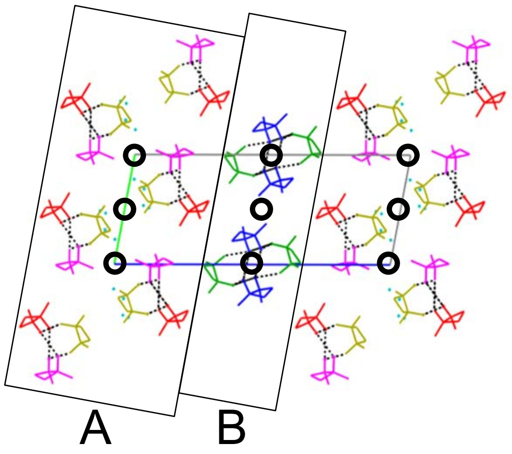
a=a
angle = 90.1°;
$b\cos\gamma/a$ =0.503



b=[120]

Projection along **a**

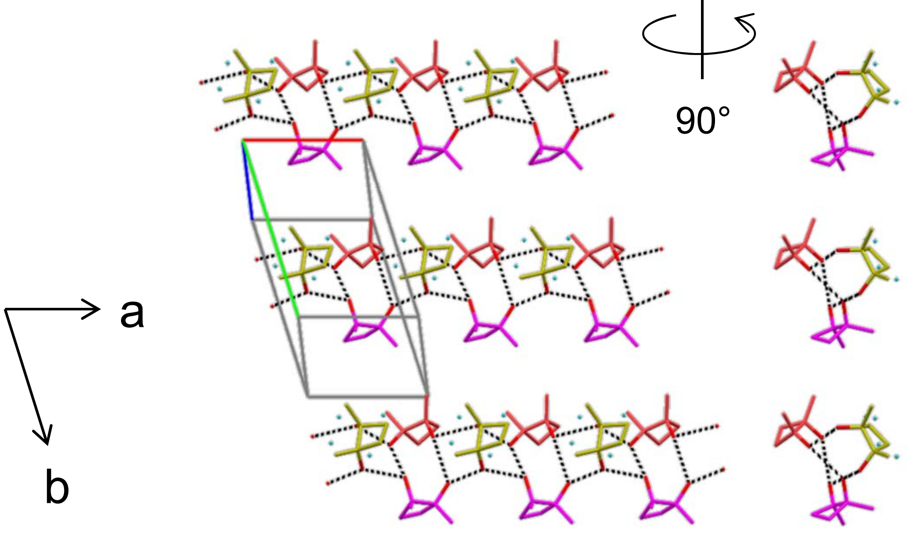




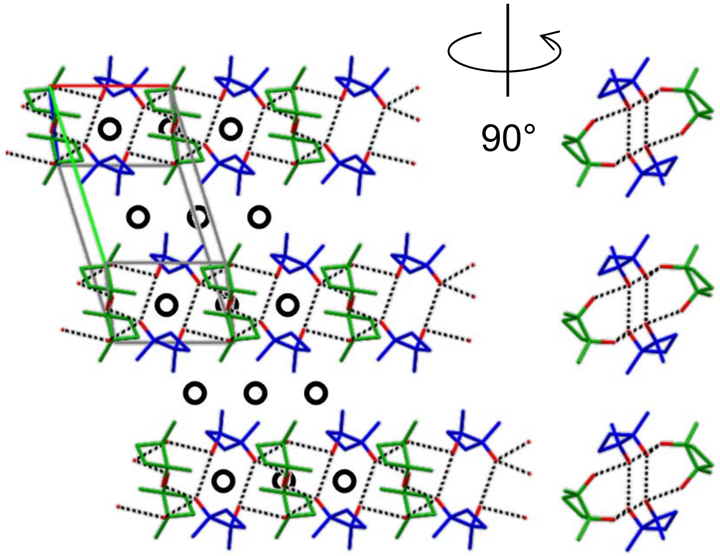
KIWVES
($P\bar{1}$, $Z'=5$)

Layers (001) A (but only one of the halves is shown) and B

$p\bar{1}$ (#2), $z'=3$
(for the full bilayer)

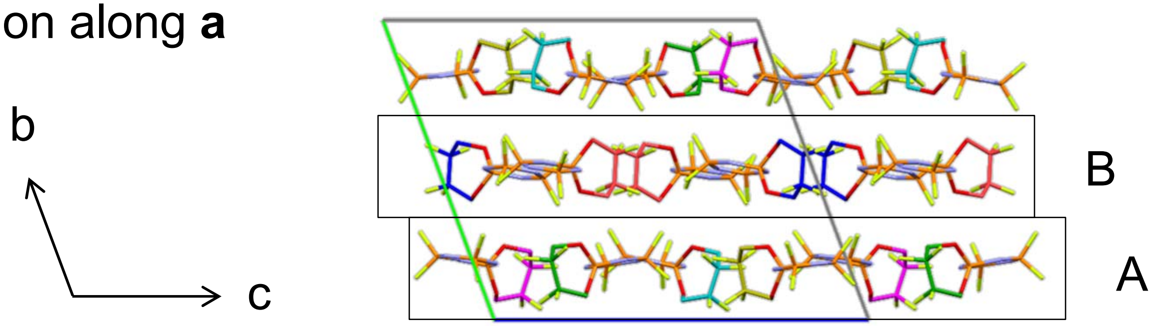


$p\bar{1}$ (#2), $z'=2$



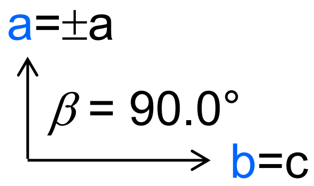
Projection along **a**

LEXVEP01
($P\bar{1}$, Z'=6)

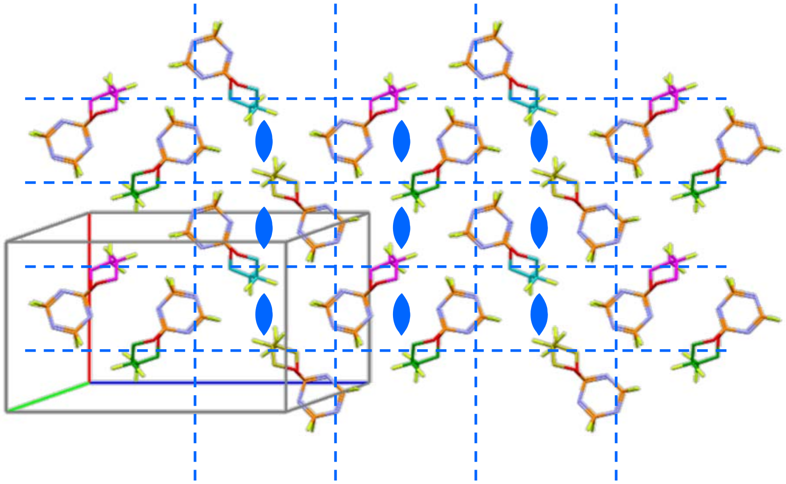


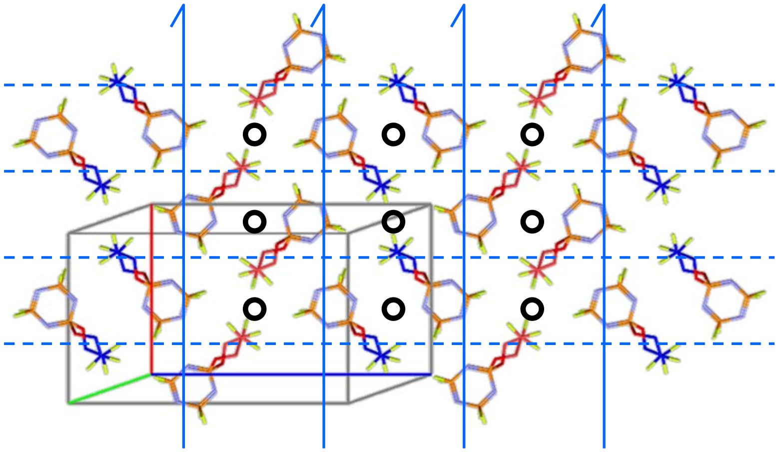
Layers (010) A and B

$pba2$ (#25), z'=1



$p2_1/b11$ (#17), z'=1
($\bar{1}s$ exact)





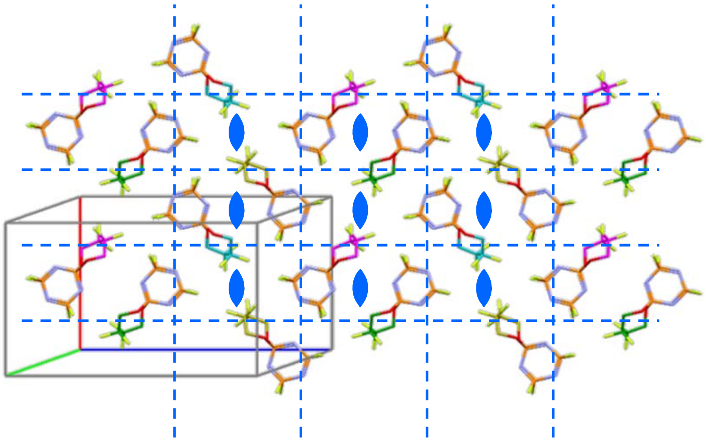
(difference between the conformational enantiomers is
the sense of twist of the $CH_2CF_2CF_2CH_2$ group)

(see also next page)

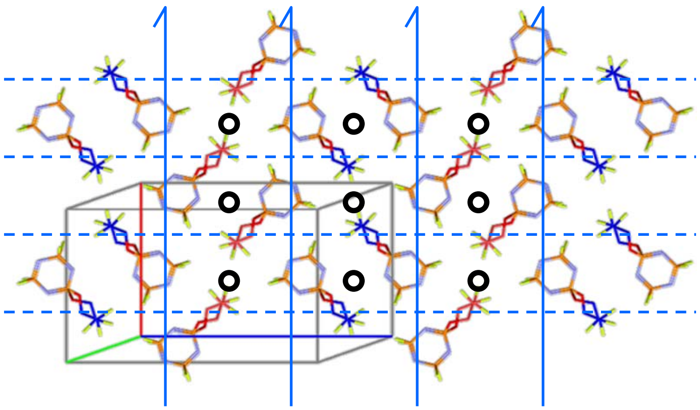
Layers (010) A and B, and their superposition

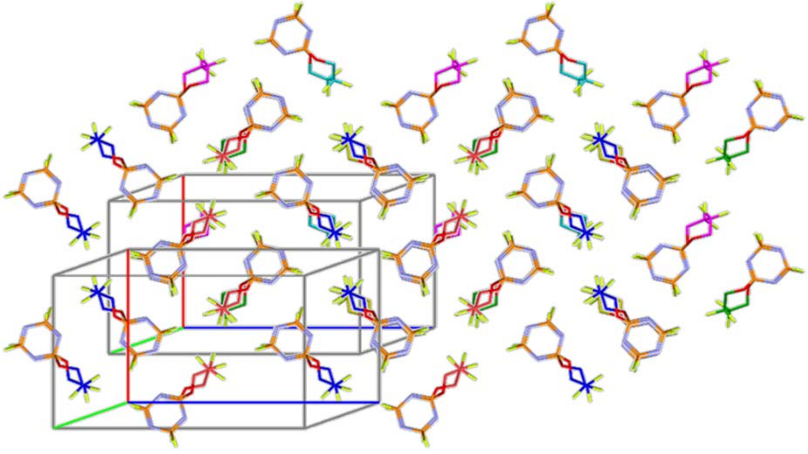
LEXVEP01,
con't
($P\bar{1}$, Z'=6)

$pba2$ (#25), z'=1



$p2_1/b11$ (#17), z'=1
($\bar{1}s$ exact)



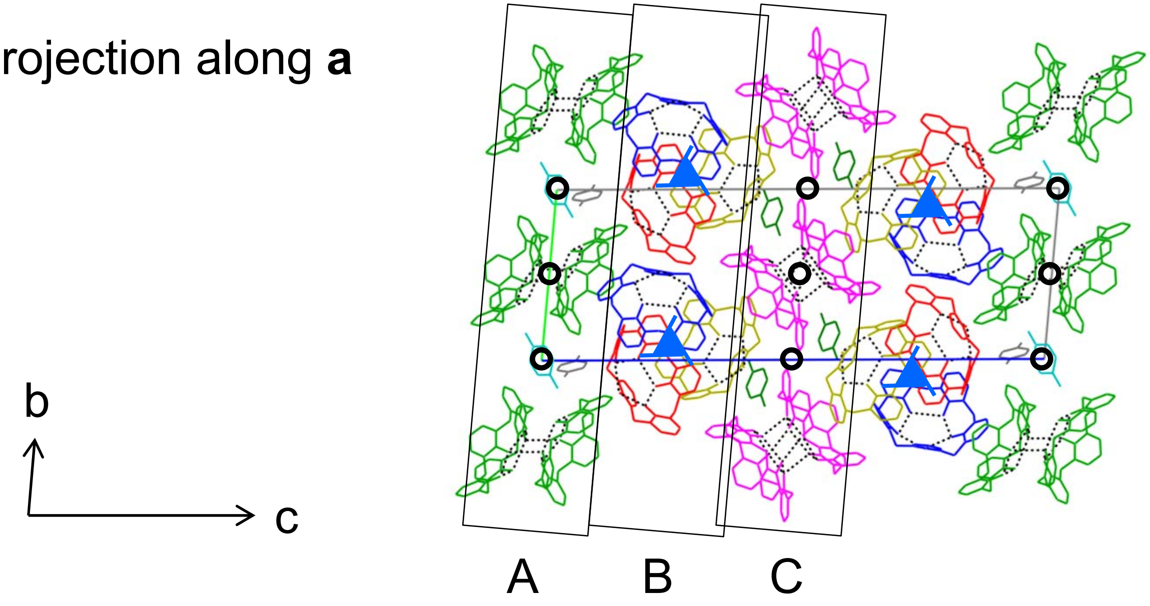


(difference between the conformational enantiomers is the sense of twist of the $CH_2CF_2CF_2CH_2$ group)

Projection along **a**

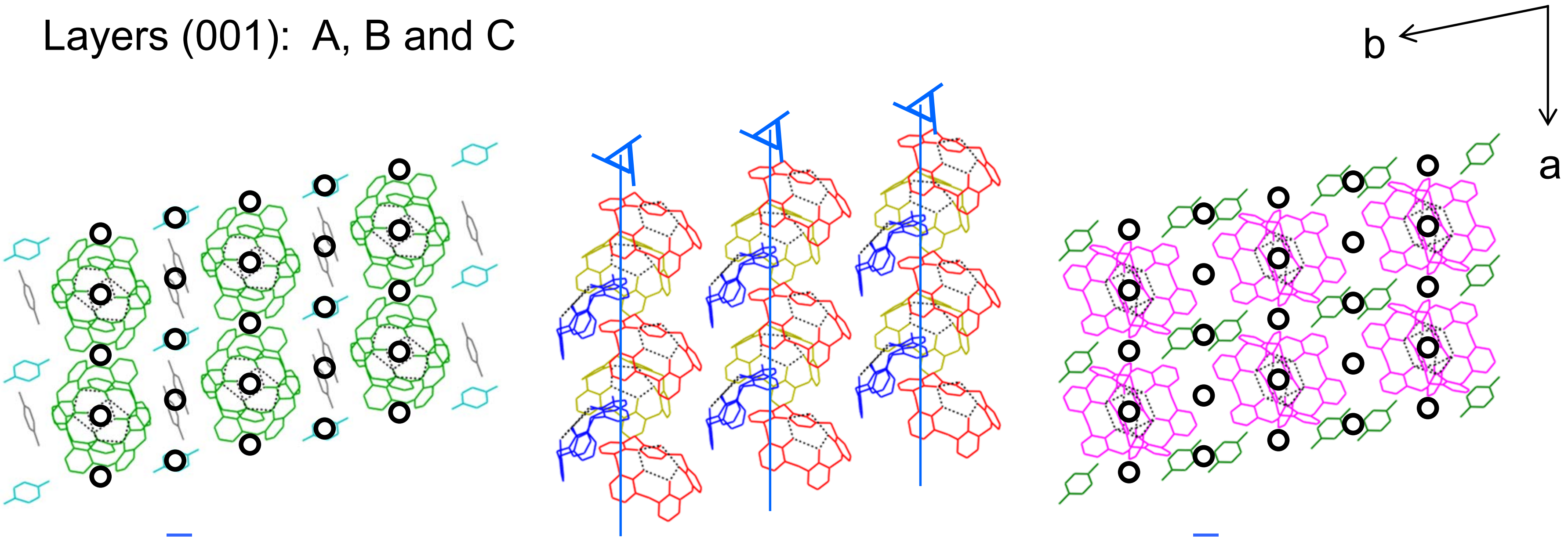
LIRXIU

($P\bar{1}$, Z'=5)



(the 3_1 axes are quite good but are necessarily local because layers cannot contain threefold axes)

Layers (001): A, B and C

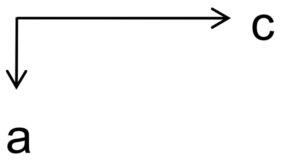


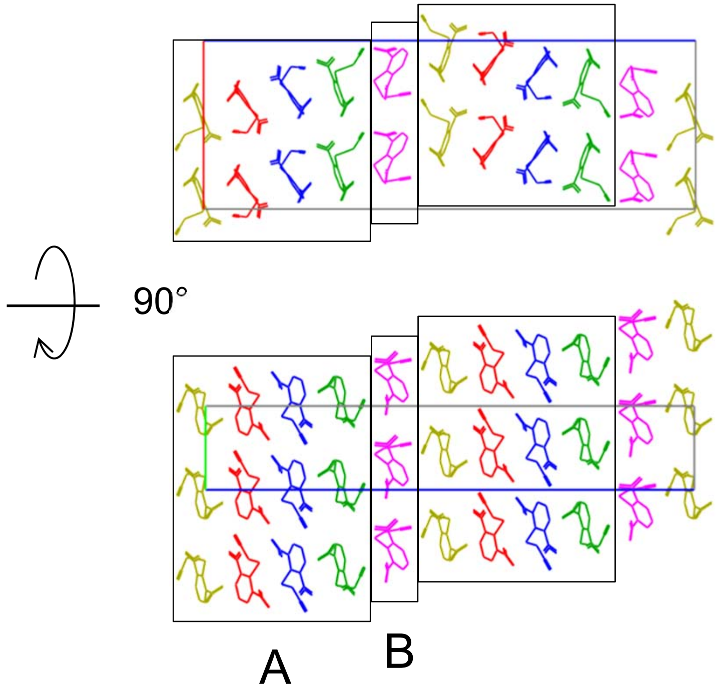
***$p\bar{1}$* (#2), *z'*=1**

***p*1 (#1), z'=3**

***$p\bar{1}$* (#2), *z'*=1**

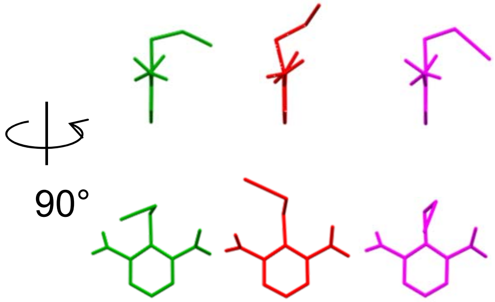
Projection along **b**





MOQJAE
($Pna2_1$, Z'=5)

The three conformations

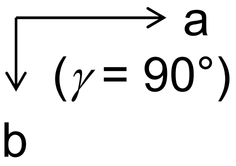


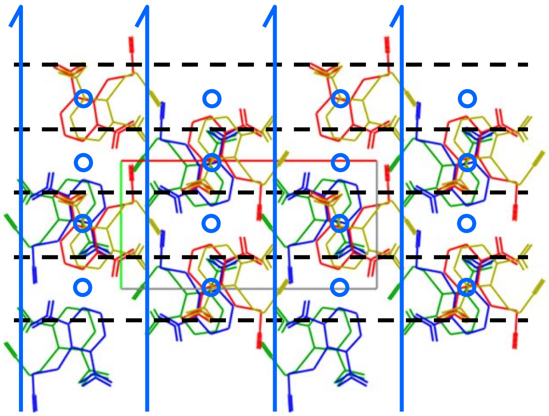
#1,4 #2,3 #5

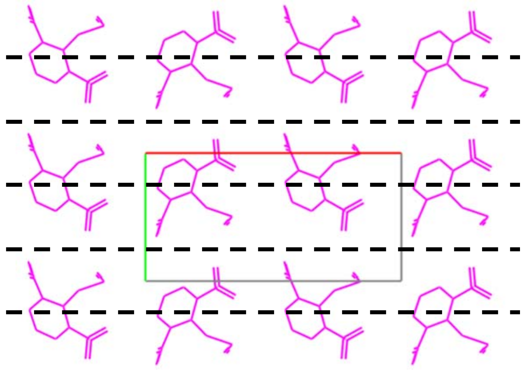
Layers (001) A and B

$p12_1/a1$ (#17), z'=2

$p1a1$ (#12), z'=1

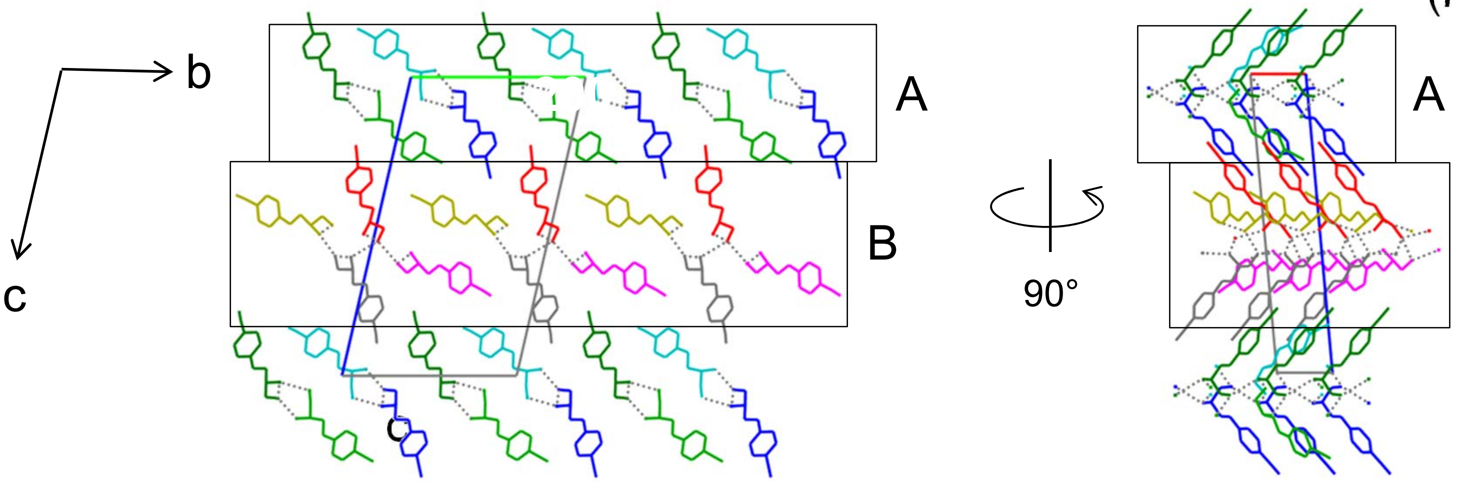






Projections along **a** and **b**

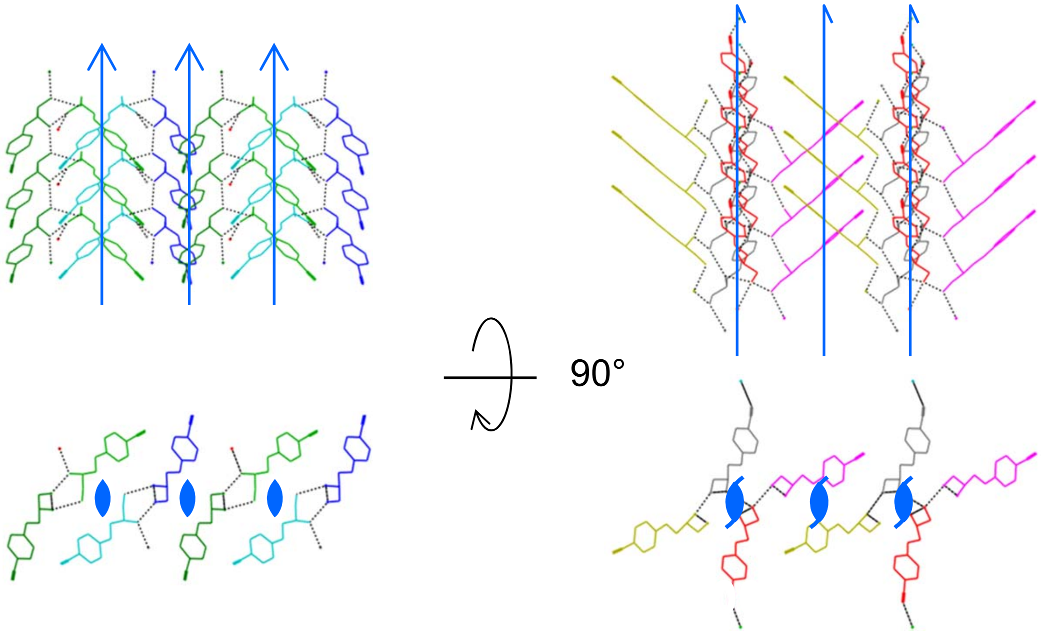
OKOXIW
($P1$, Z'=8)



Layers (010) A and B

a=a
↑ γ = 90.0°
→ b=b

(not approximately C2
because β = 94.9°)

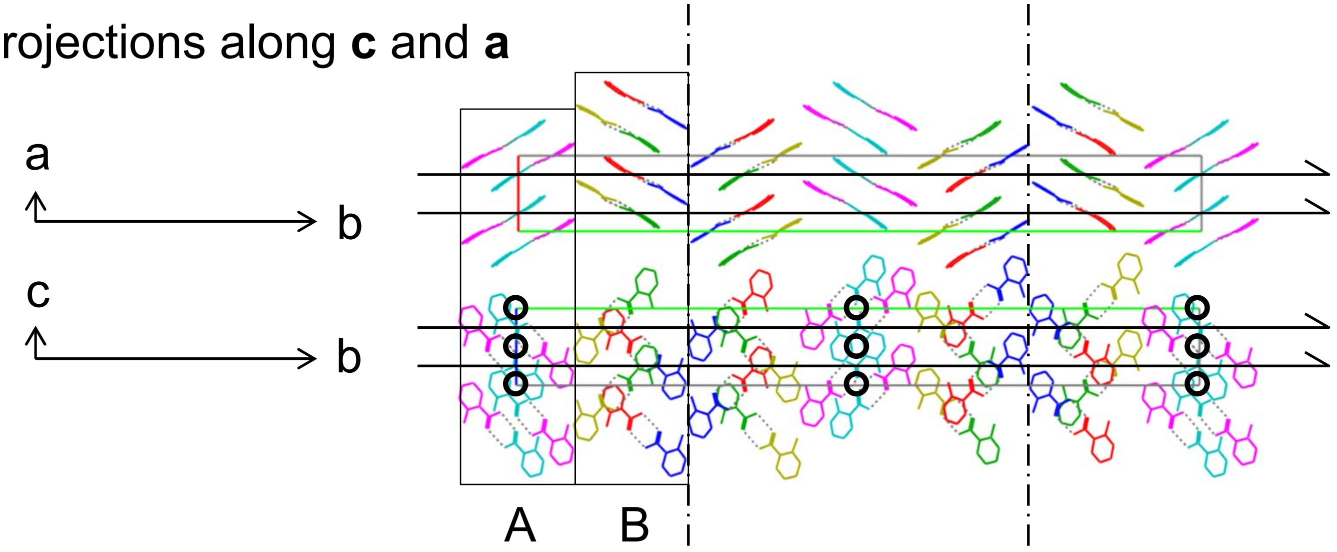


***p*211 (#8), *z*'=2**

***p*$2_1$11 (#9), *z*'=2**

Projections along **c** and **a**

OTOLIC04
($P2_1/n$, Z'=6)

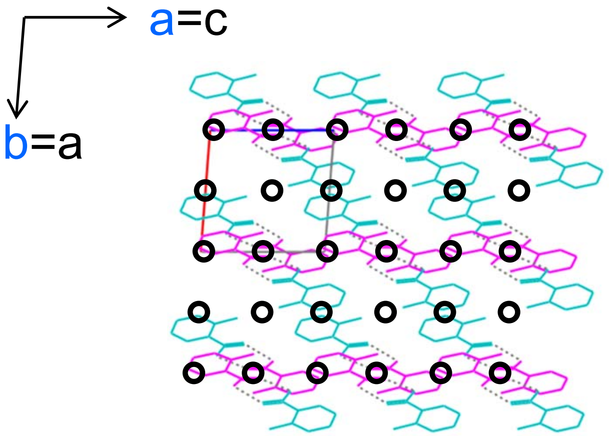


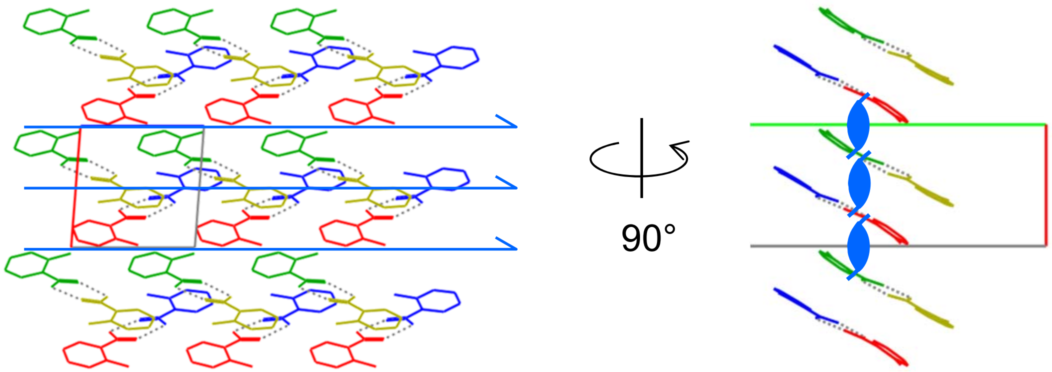
(β = 94.4°)

Layers (010) A (all dimers parallel) and B (two dimer orientations)

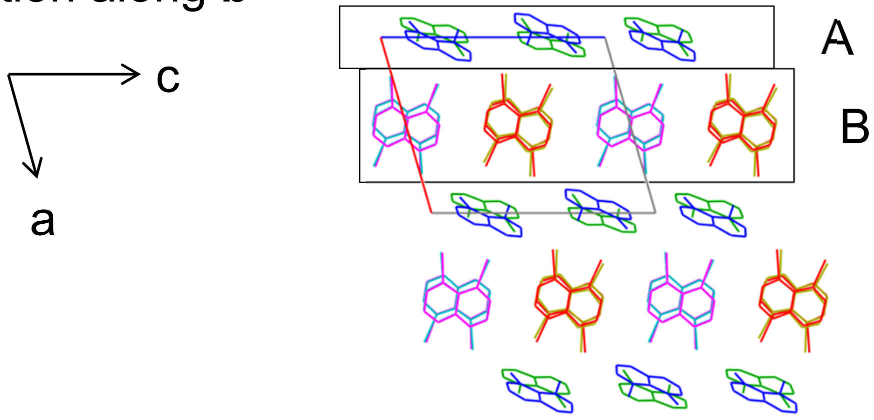
$p\bar{1}$ (#2), z'=3

$p2_111$ (#9), z'=2

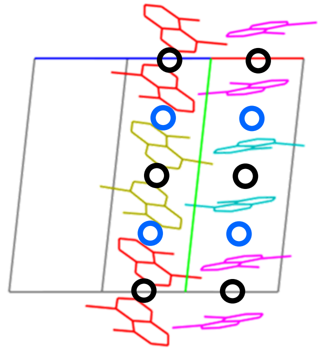




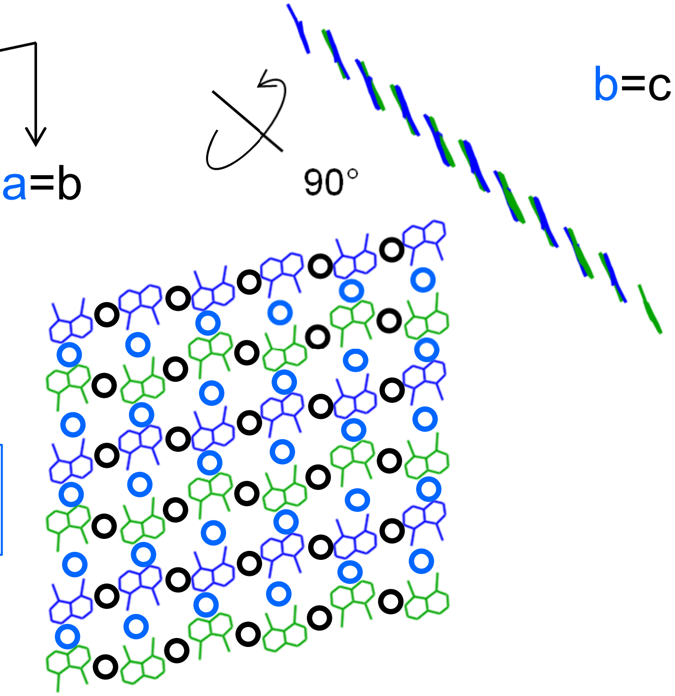
Projection along **b**



PIPQUA
($P\bar{1}$, Z'=6)

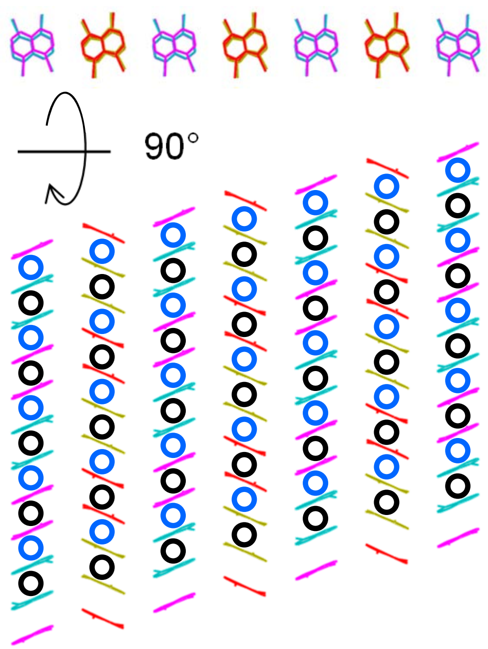


Layers (100) A and B



$a\bar{1}$ (#2), z'=1

pseudo
a centering

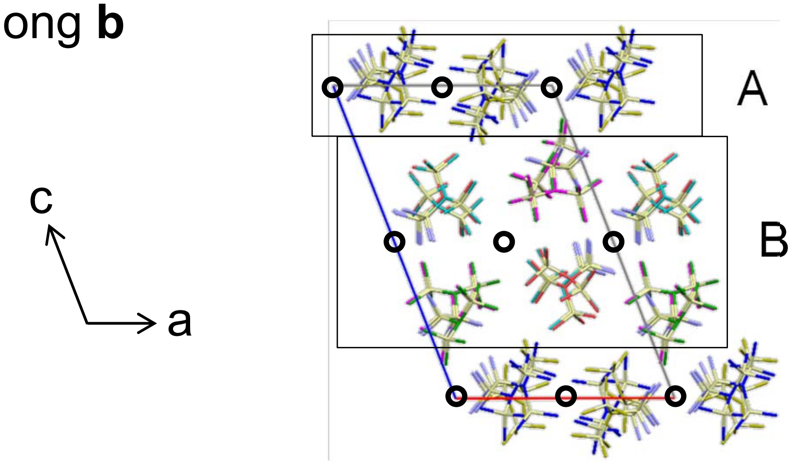


$p\bar{1}$ (#2), z'=2

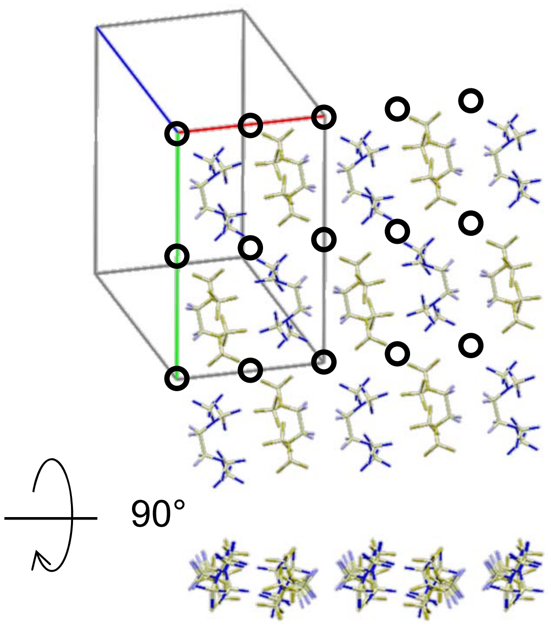
pseudo
translation
b/2

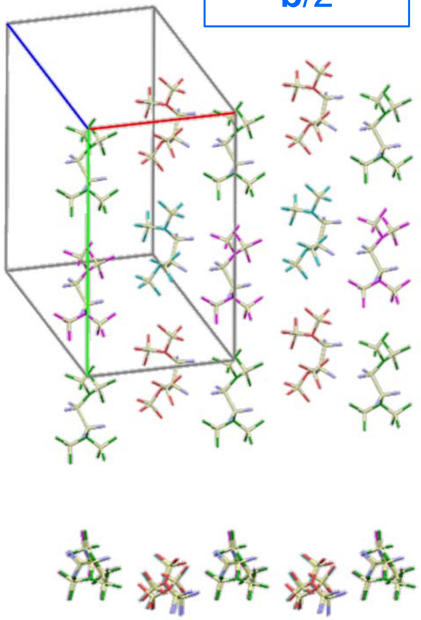
QUJSAP
(*P*$\bar{1}$, *Z*'=6)

Projection along **b**



Layer A and half of layer B





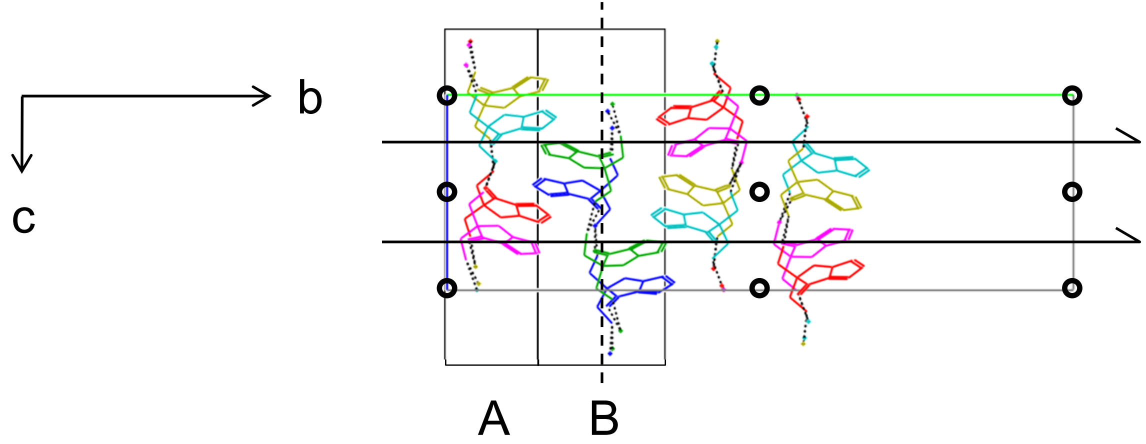
pseudo translation **b**/2

Layer B has a **b**/2 pseudotranslation; layer A does not.
Both layers have crystallographic inversion centers; layer B also has approximate inversion centers.

Inversion centers are not shown for B because they are between the two layer halves. The picture shown is intended to show the approximate translation.

Projection along **a**

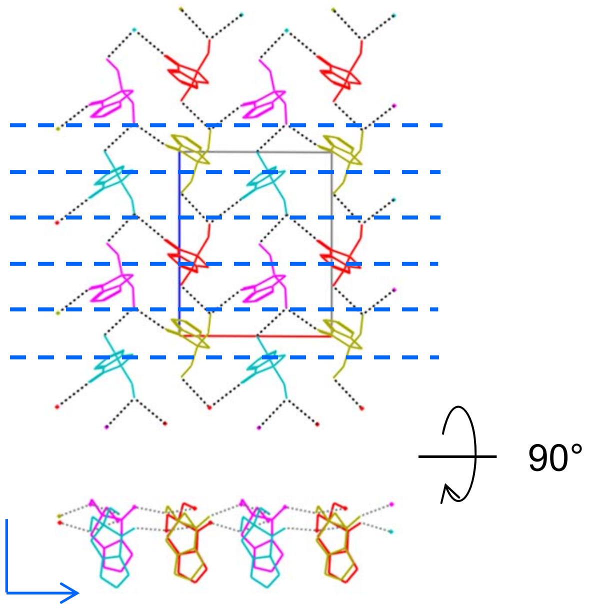
QUYNUU
($P2_1/c$, Z'=6)



Layers (010) A and B

***pb*11 (#12),**
***z'*=1**

pseudo
translation
c/2

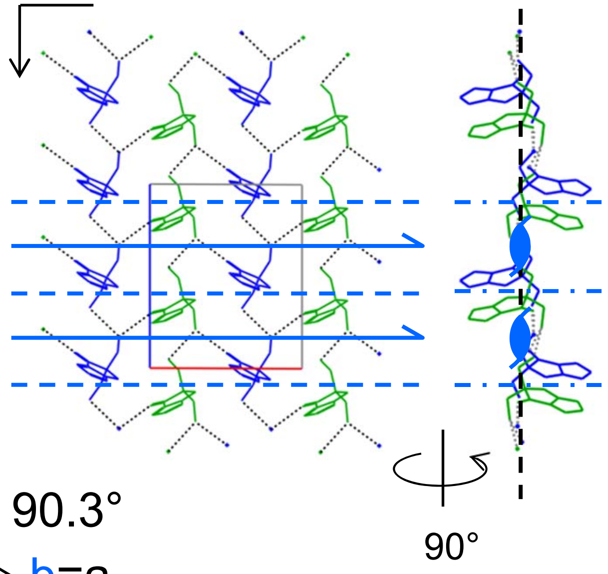


a=c/2

β = 90.3°

b=a

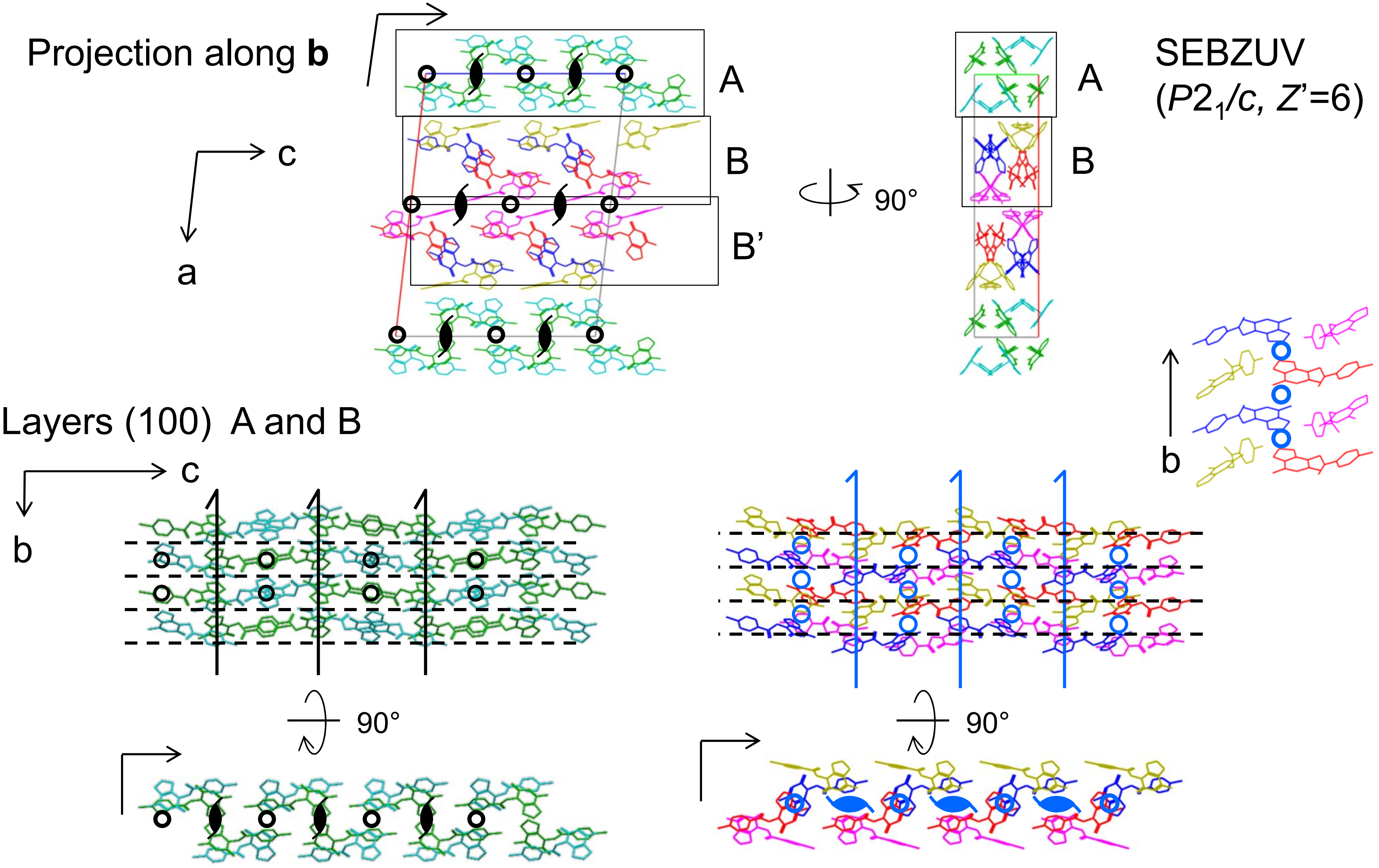
***pb*2$_1$*a*,**
***z'*=1**



a=c

β = 90.3°

b=a



Projection along **b**

SEBZUV ($P2_1/c$, Z'=6)

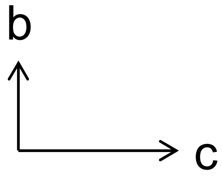
Layers (100) A and B

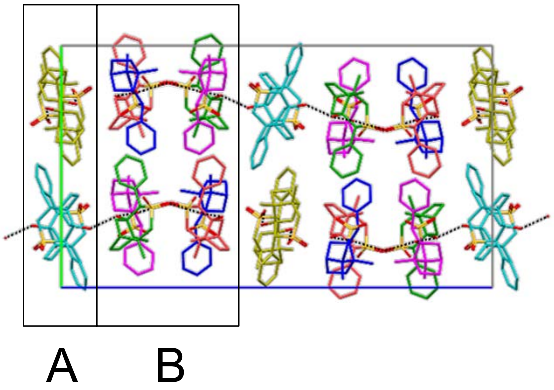
(the local 1-bar sites are at y = 0.40 and 0.60 so that the translations for the 2_1 axes are not ½)

$p12_1/c1$ (#17), z'=1

$p12_1/c1$ (#17), z'=2

Projection along **a**

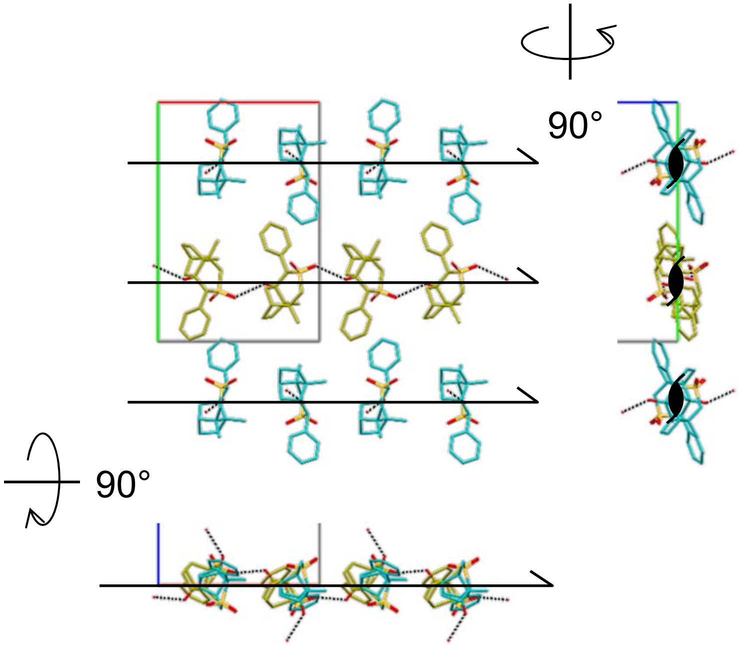


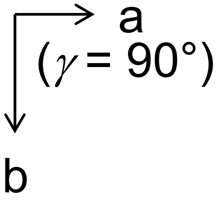


UYOPAA
($P2_12_12_1$, Z'=6)

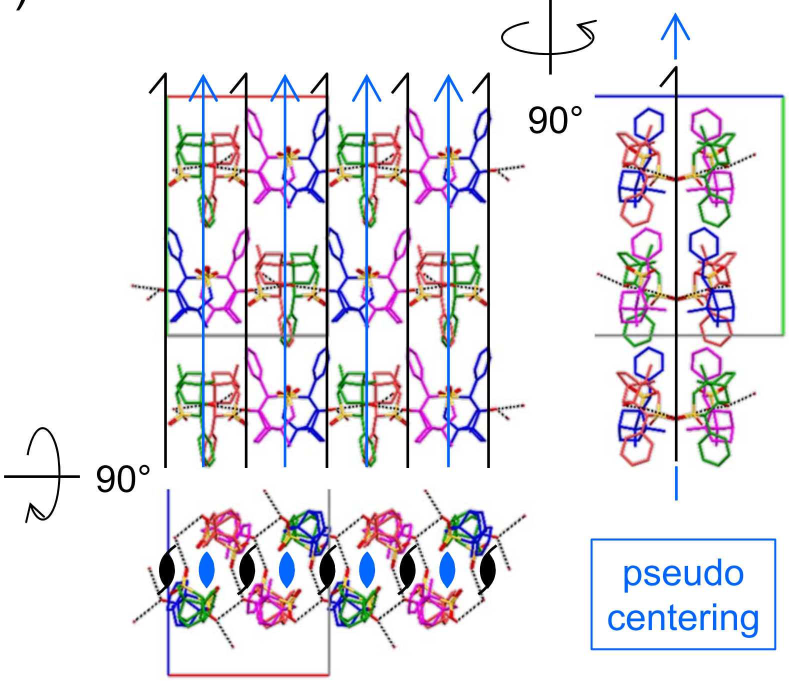
Layers (001) A and B

$p2_111$ (#9), z'=2



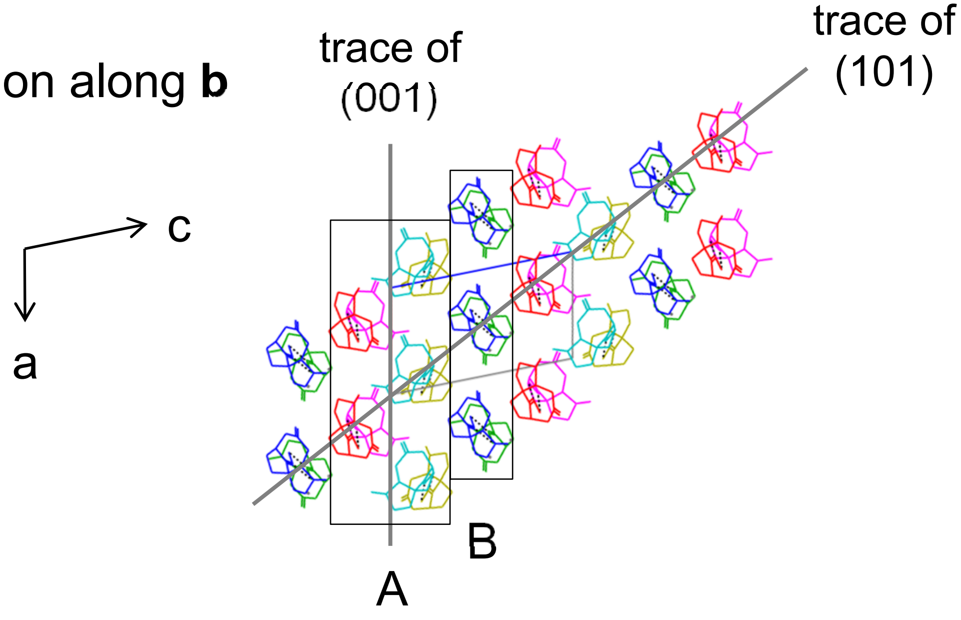


$c121$ (#10), z'=2



pseudo centering

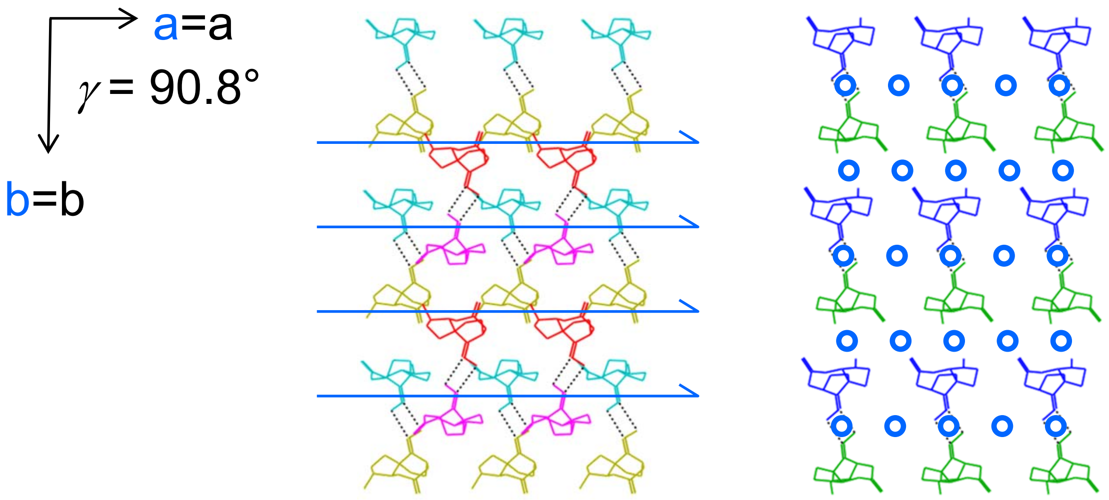
Projection along **b**



WIYSAZ
(*P*1, *Z*'=6)

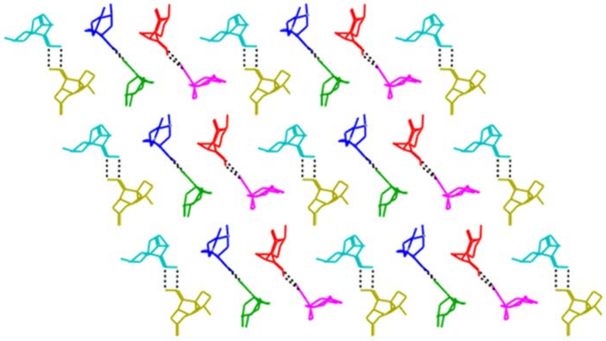
(Z'=5+1 is a better description than Z'=6 because molecule #2 is the "other" enantiomer, which is disordered *ca* 1:1 with a diastereomer having the Me group up rather than down)

Layers (001) A and B



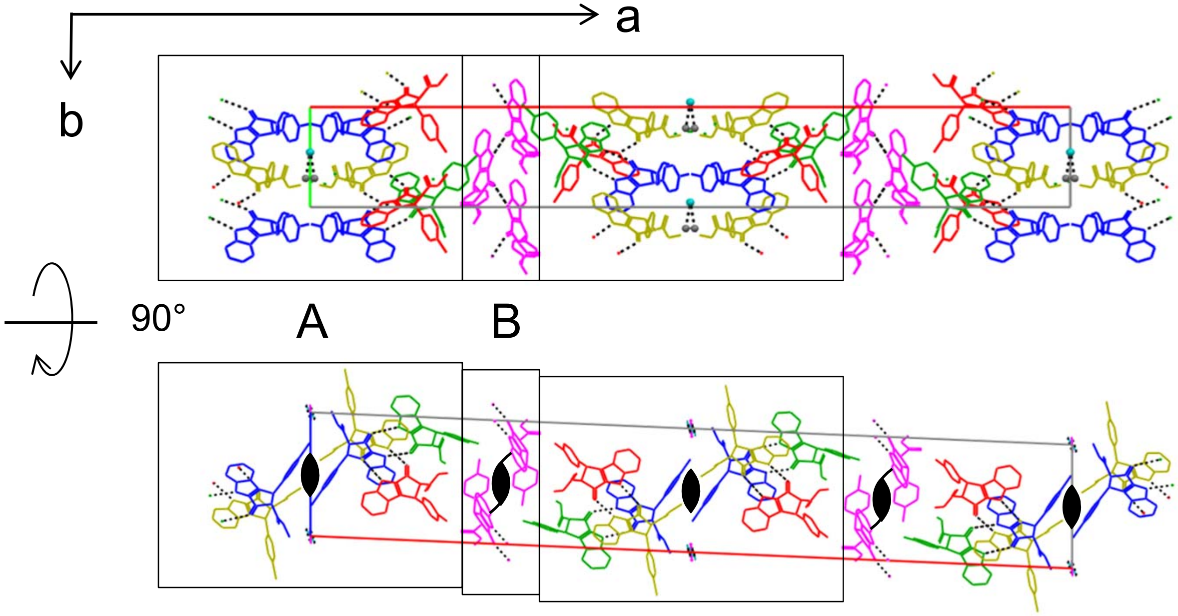
***p*2$_1$11 (#9), *z*'=2** ***p*$\bar{1}$ (#2), *z*'=1**

Layer (101)
(no pseudosymmetry)



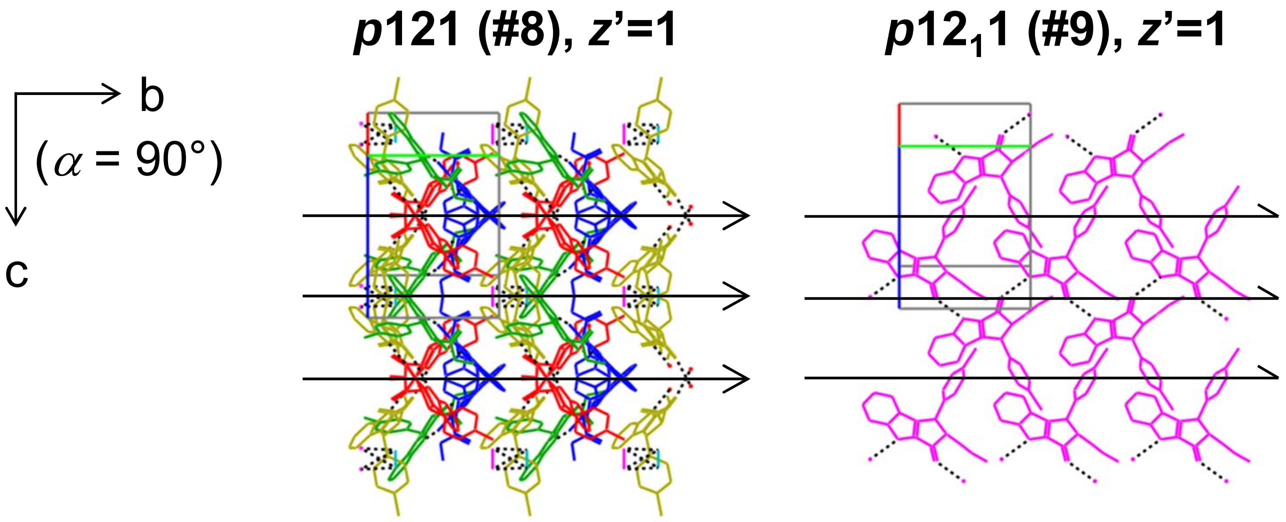
Projection along **c**

YAJJEA
($C2$, $Z'=5$)



(In the CSD entry the disordered H2Os at x=0 and ½ are residues #5, 6 and the fifth organic molecule is #7. Numbers have been changed so that the water molecules are #6,7 and the fifth organic molecule is #5.)

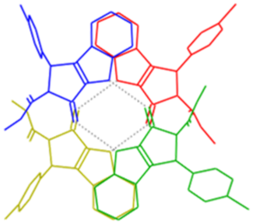
Layers (100) A and B



$p121$ (#8), $z'=1$

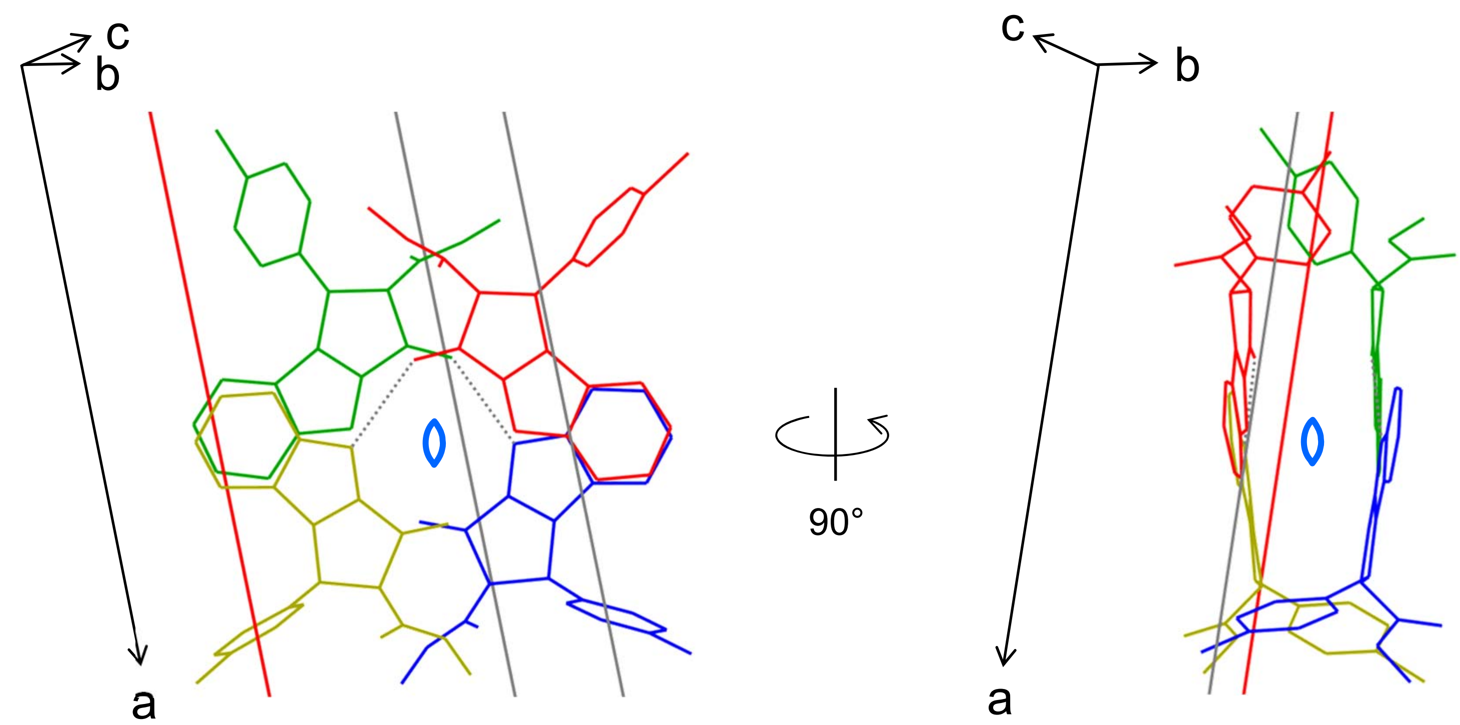
$p12_11$ (#9), $z'=1$

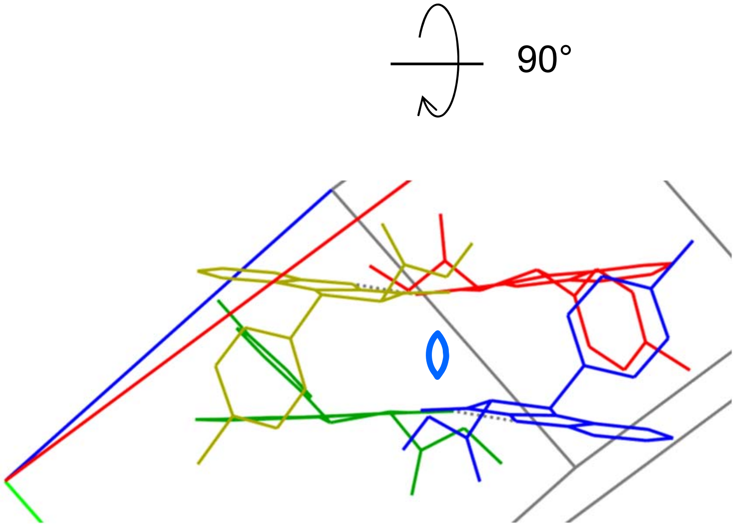
Dimer pair
(local symmetry 222)



(see also next page)

YAJJEA, con’t (*C*2, *Z*’=5)

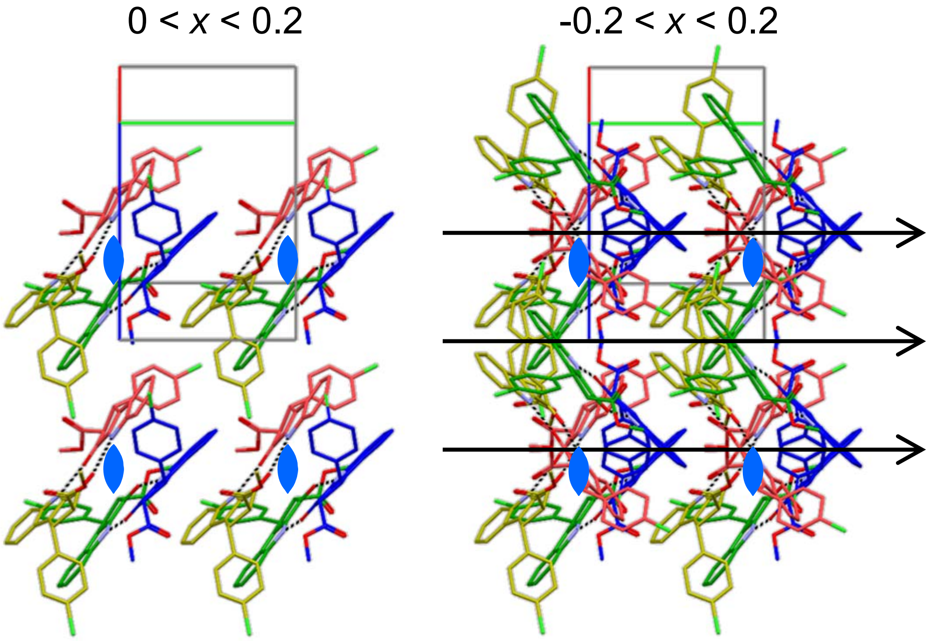




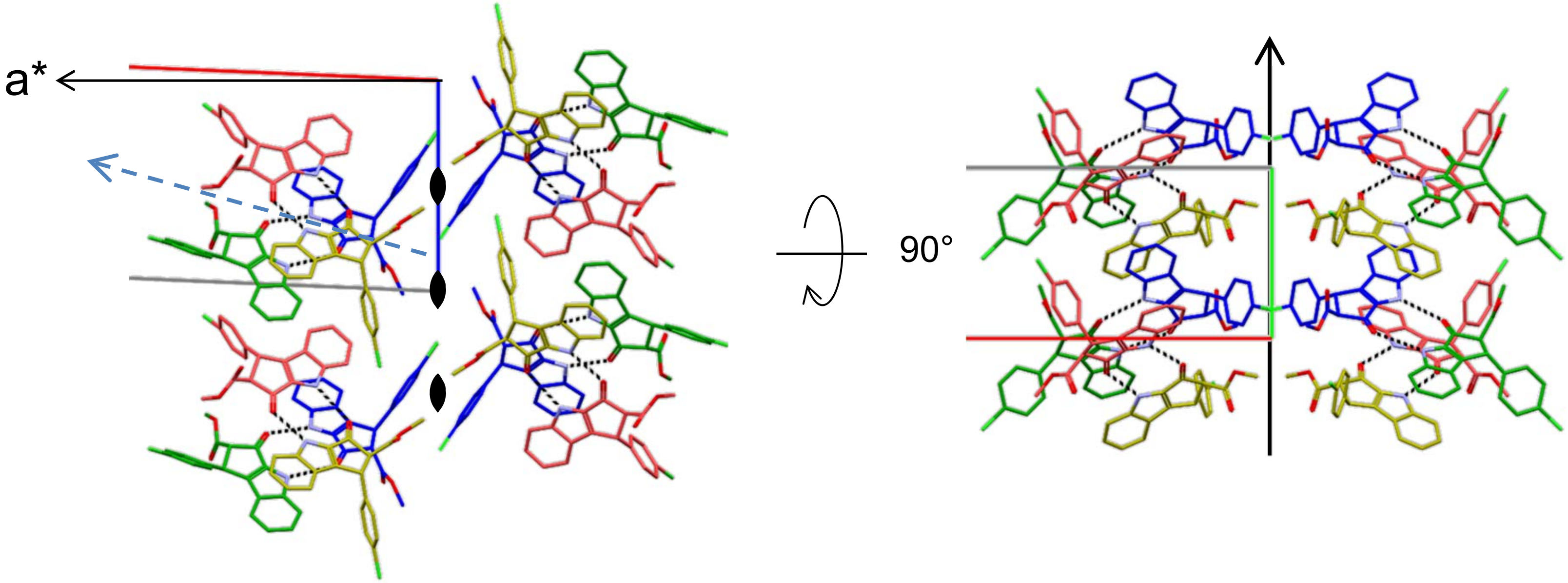
Local twofold axes are not well aligned with any simple vector [*uvw*]

YAJJEA, yet again (*C*2, *Z*'=5)

Views along **a***

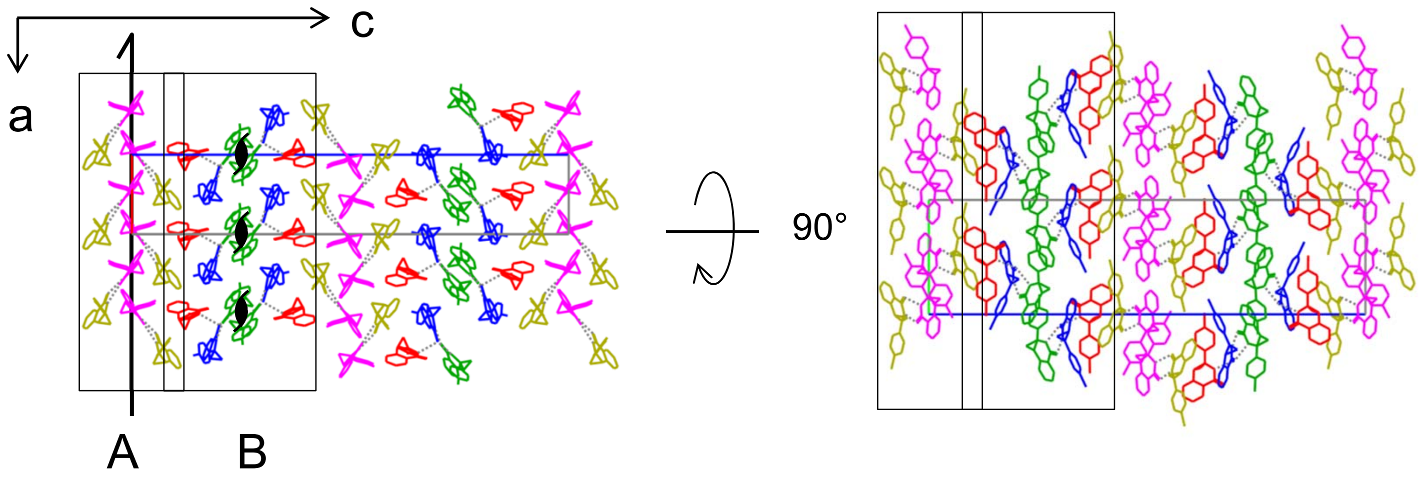


Local approximate axes 2 are not aligned with the crystallographic 2s, with **a**, or with **a***.

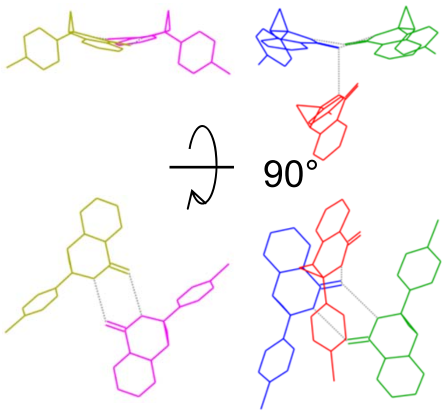


YUKLIB
($P2_12_12_1$, Z'=5)

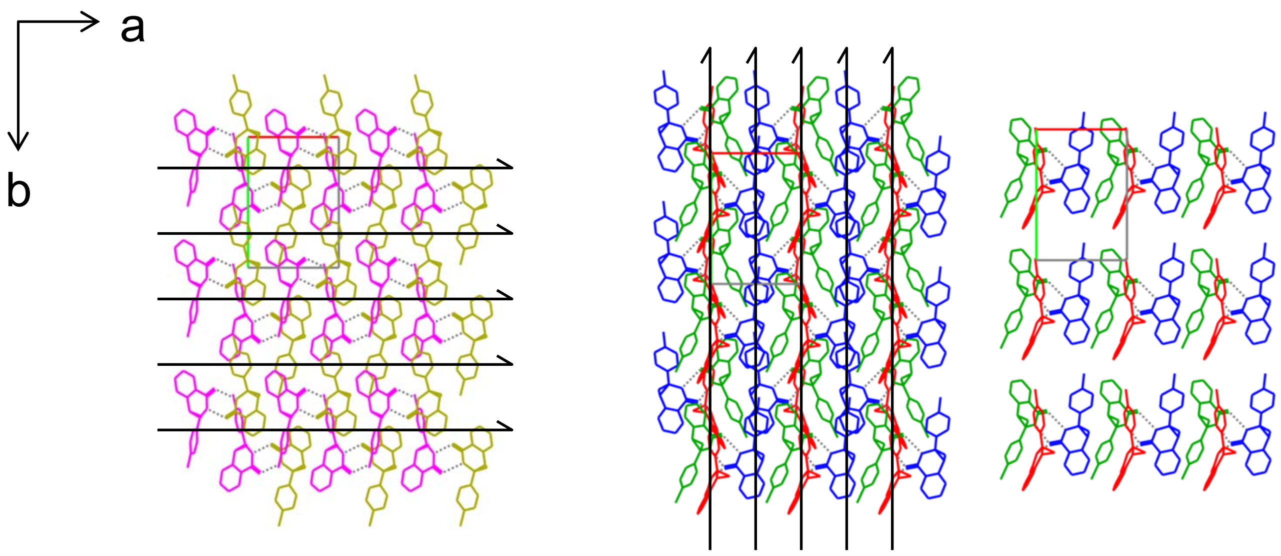
Projection along **b**



The H-bonded units



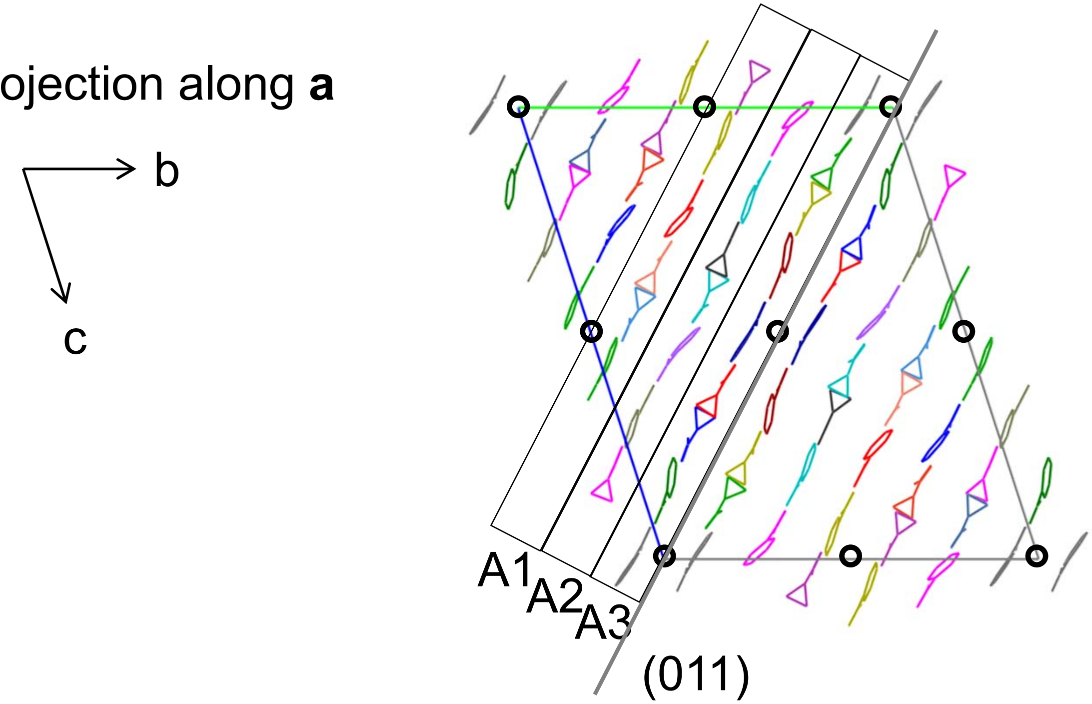
Layers (001) A, B, and a half layer of B near *x* = ¼



$p2_111$ (#9), z'=2

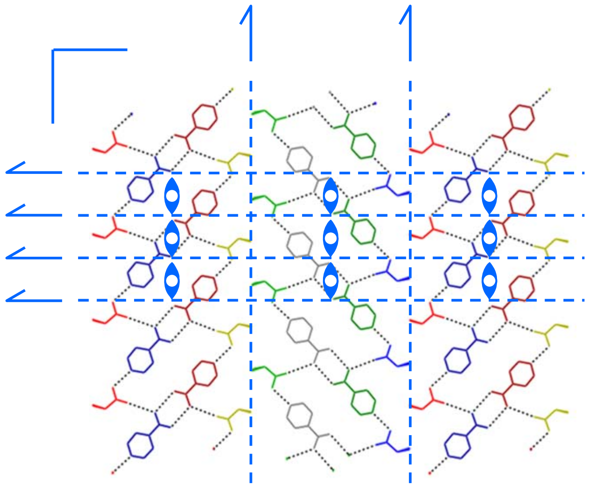
$p12_11$ (#9), z'=3

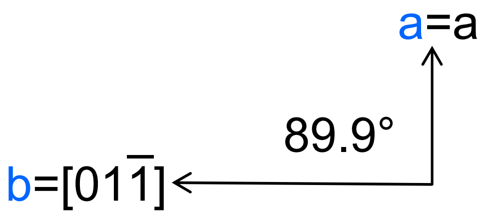
Projection along **a**



ACOMOW
($P\bar{1}$, Z'=12)

Overlay by translation of the three independent layers (011)





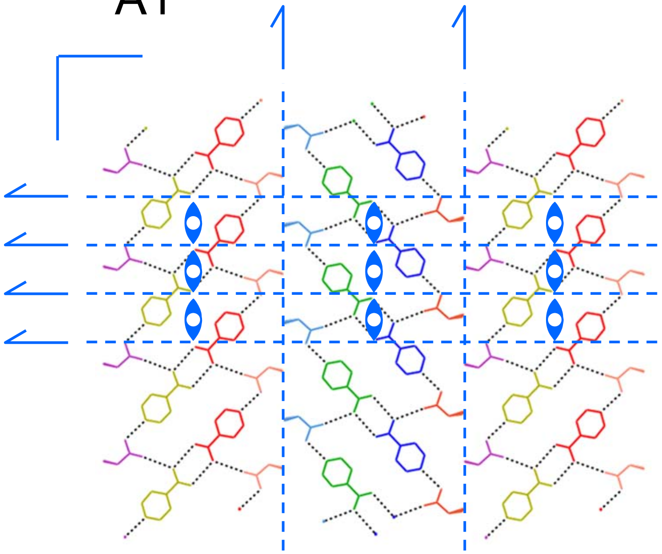
***pbam* (#44), *z'*=1**

(see also
next page)

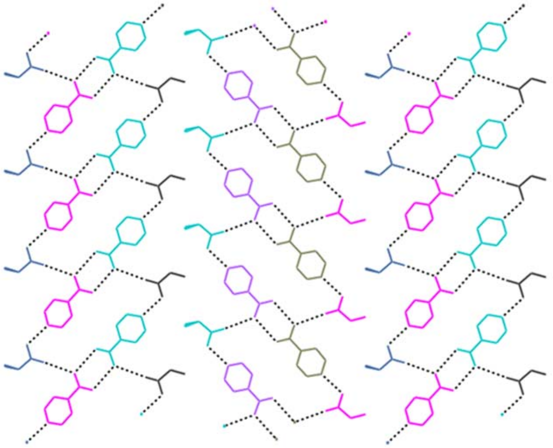
The three (011) layers

ACOMOW,
con’t
($P\bar{1}$, Z'=12)

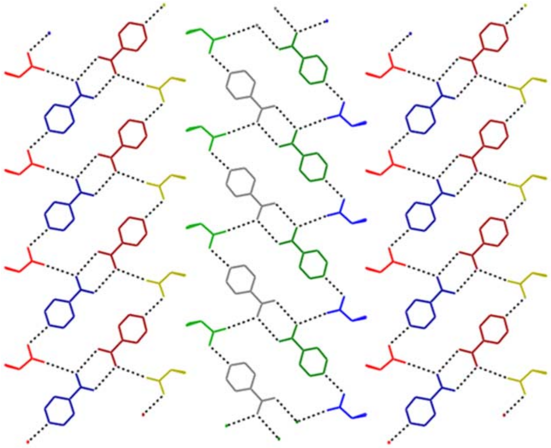
A1



A2

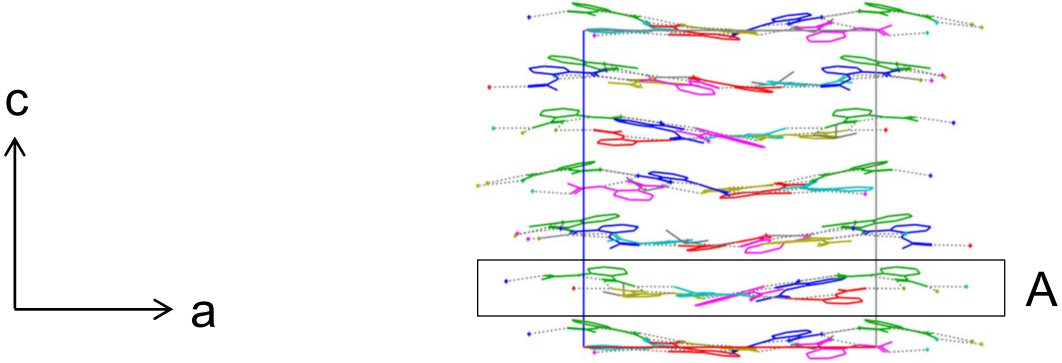


A3

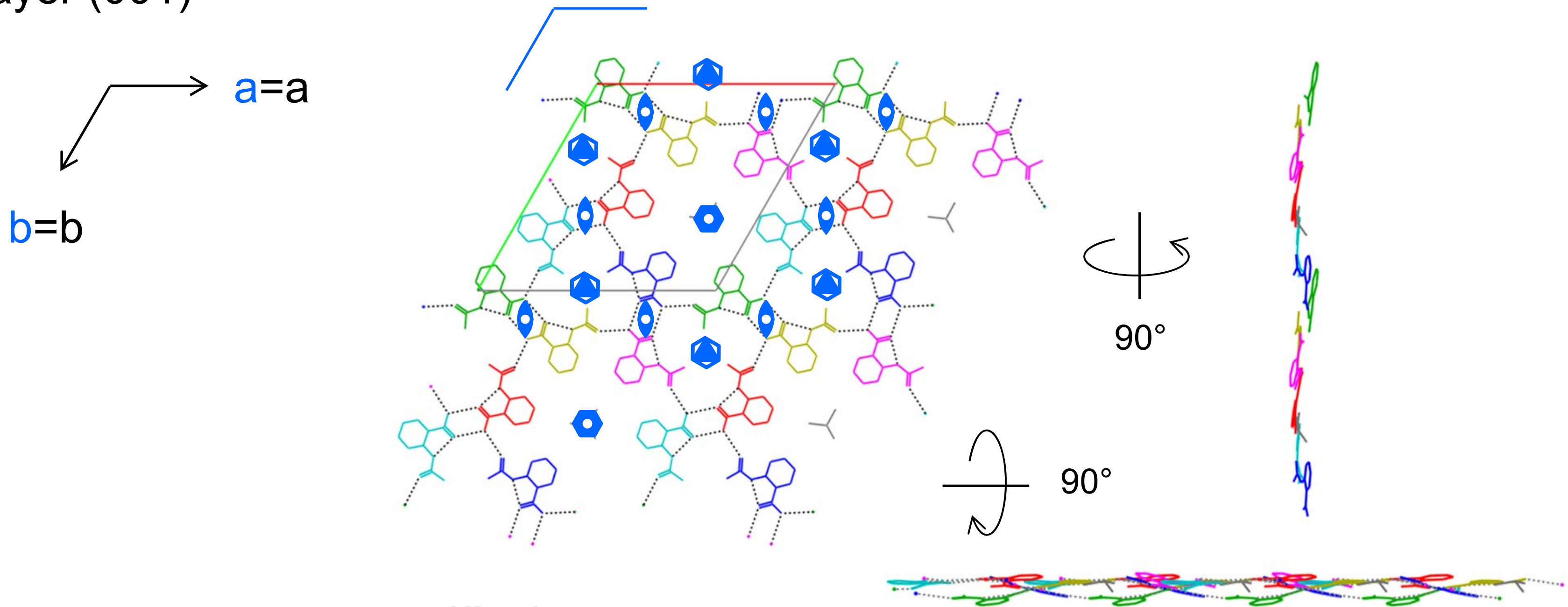


Projection along **b**

CEGBAS
($P6_1$, $Z'=6$)



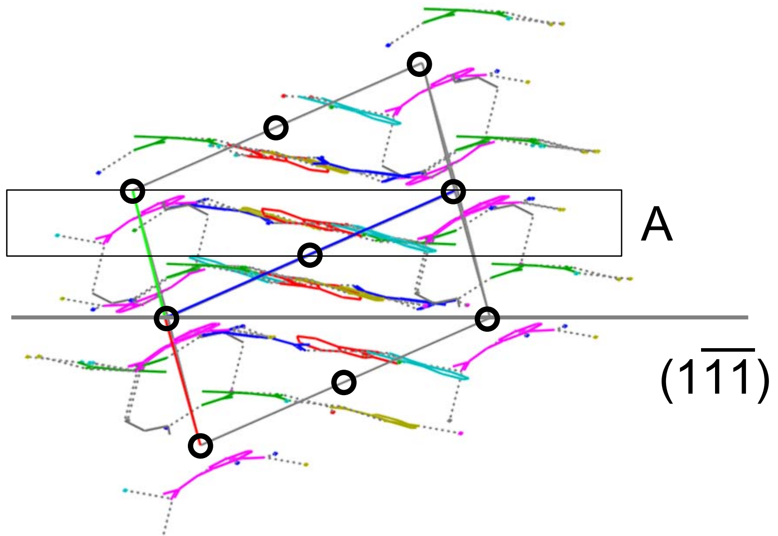
Layer (001)



***$p6/m$* (#75), *z'*=1**

Projection along [110]

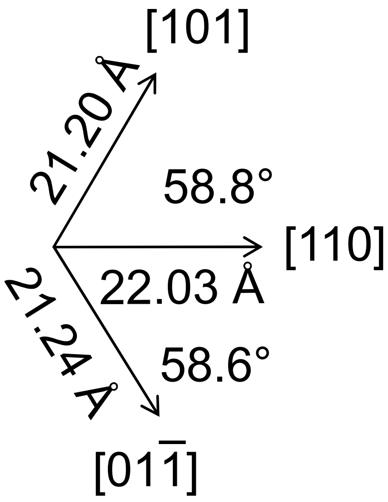
CEGBEW
($P\bar{1}$, Z'=6)

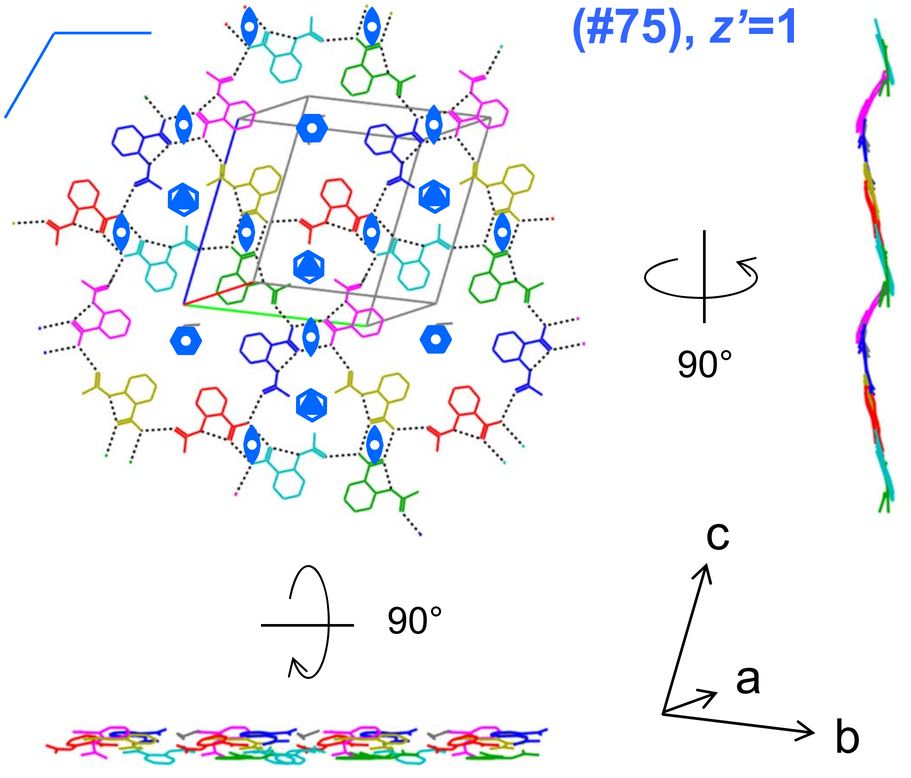


Layer $(1\bar{1}\bar{1})$

$p6/m$
(#75), z'=1

Same layer as in CEGBAS but more buckled

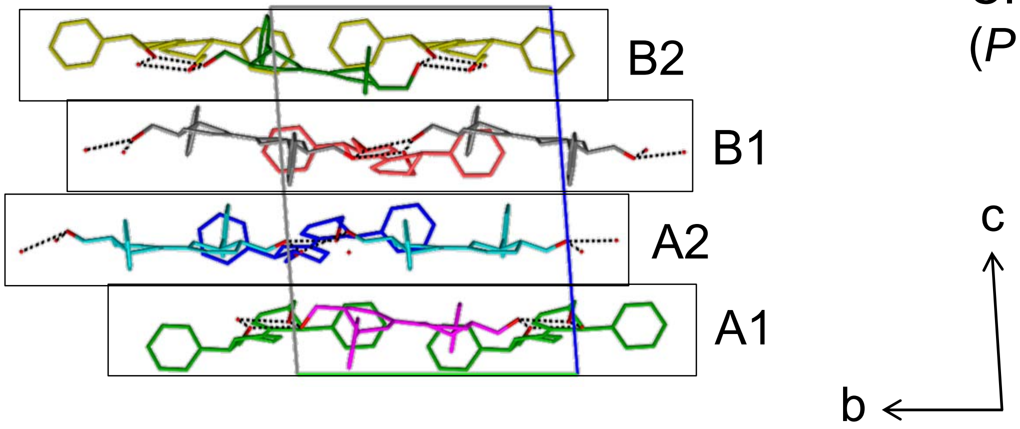




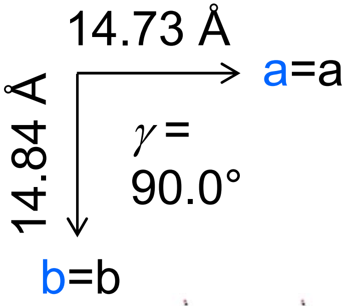
(H bonds to adjacent layers not shown)

Projection along **a**

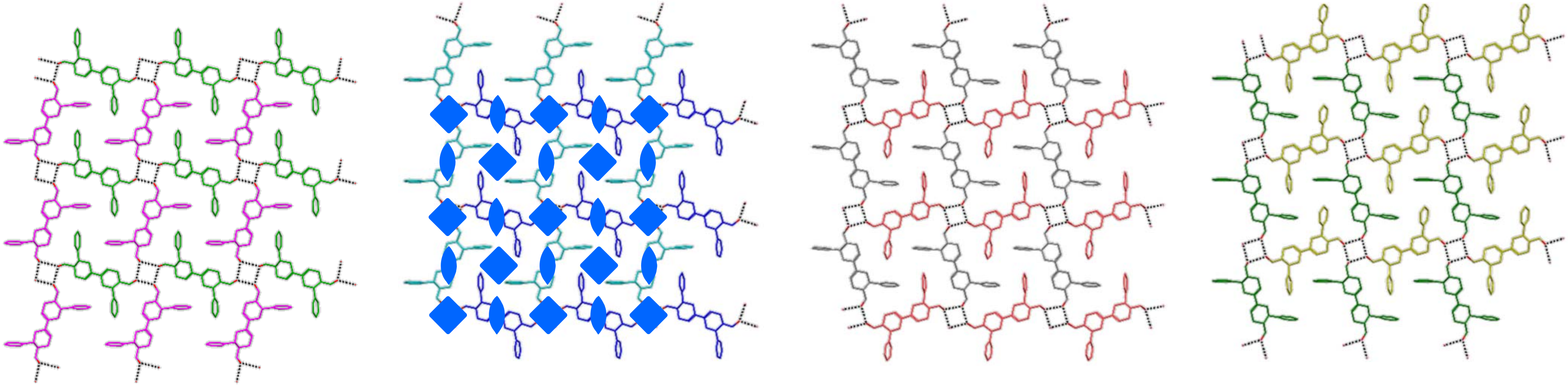
CICTIT
(*P*1, *Z*'=8)



Layers (001) A1, A2, B1, B2



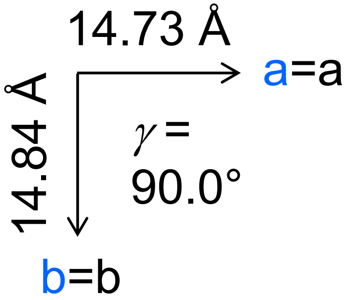
***p*4 (#49), *z'*=1/2**



(superposition of layers is shown on the next page)

Layers (001)

CICTIT,
con’t
($P1$, Z’=8)


14.73 Å

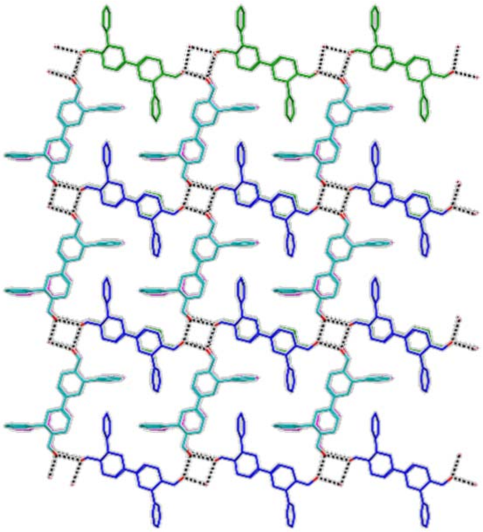
a=a

14.84 Å

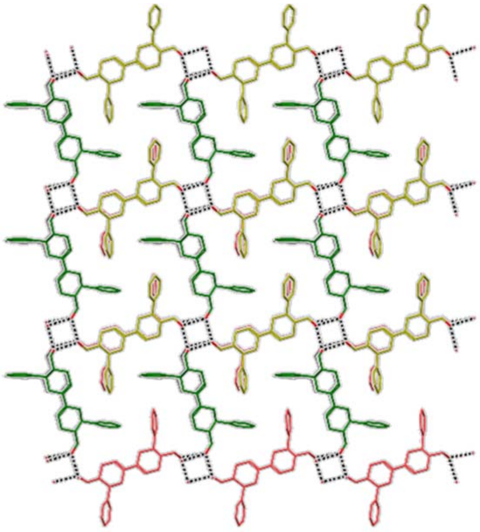
γ =
90.0°

b=b

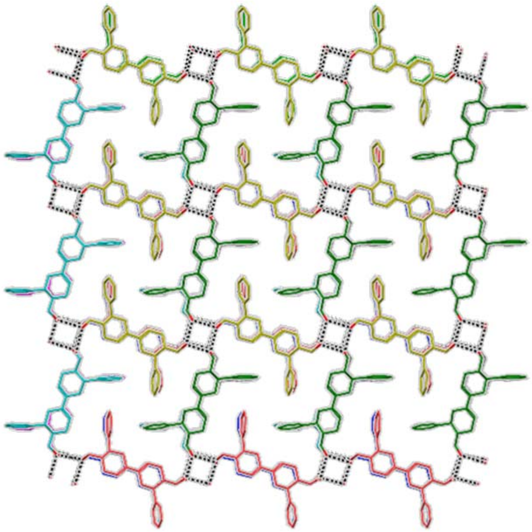
Superposition by
translation of A1 and A2



Superposition by
translation of B1 and B2

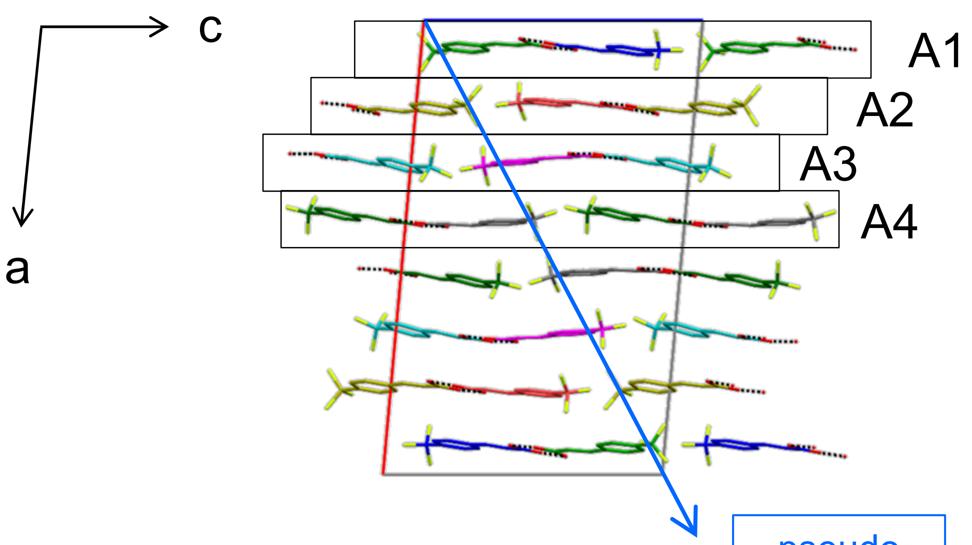


Superposition of all four
after rotation of B1, B2
by 180° around b=b

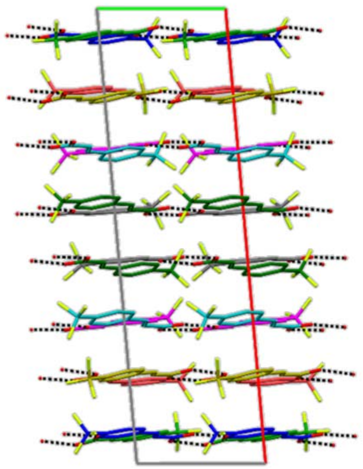


Projections along **b** and **c**

COCMIR02
$(P\bar{1}, Z'=8)$



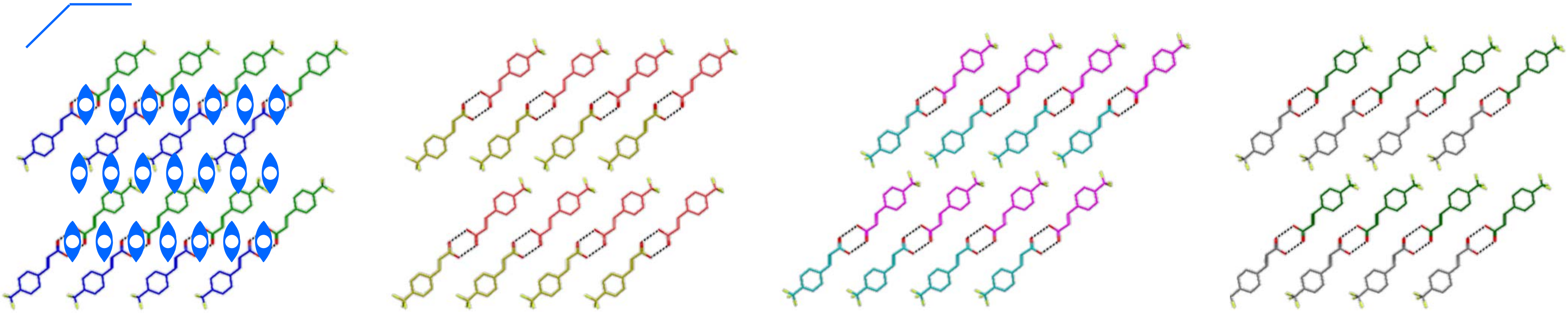
pseudo translation [101]/4



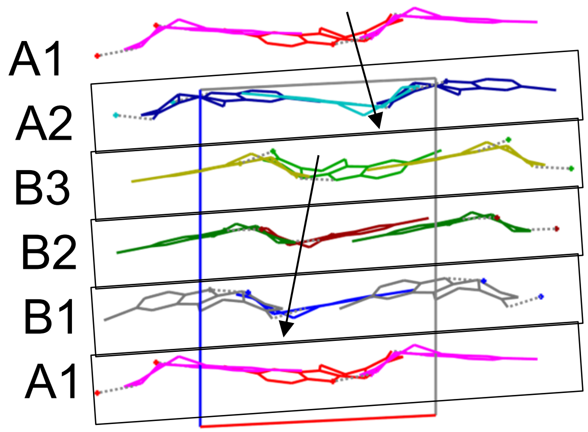
COCMIR02 was determined at 120 K. COCMIR (200 K) and COCMIR01 (145 K) have the same layers but no pseudotranslation.

Layers (100) A1, A2, A3, A4

***p*112/*m* (#6), *z'*=1**



Projection along **b**

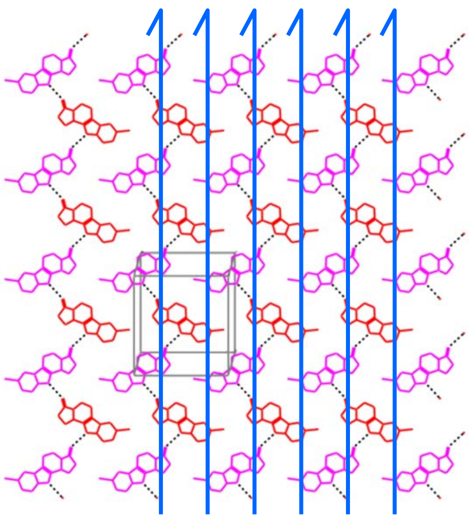


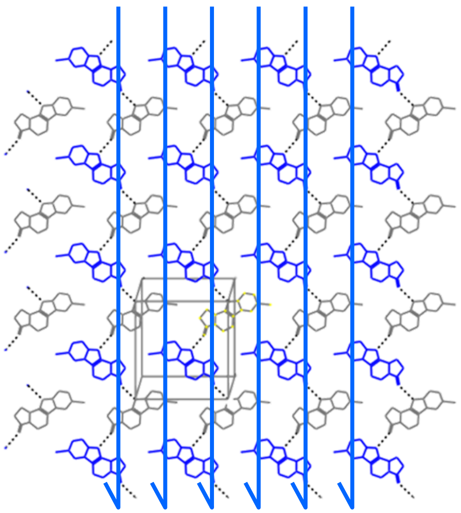
COVBEV
($P1$, Z'=10)

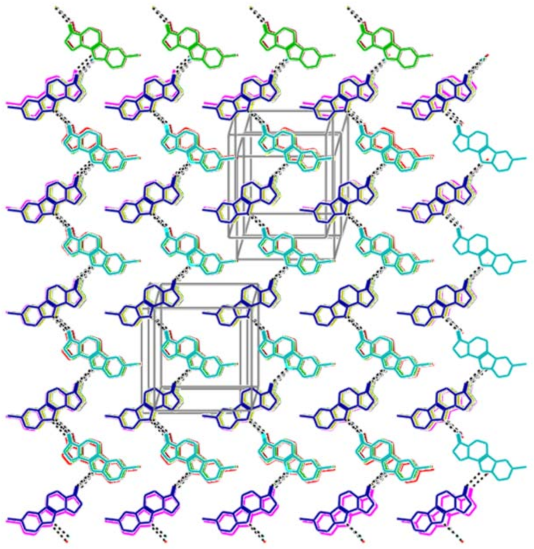
Layers (0 0 1)

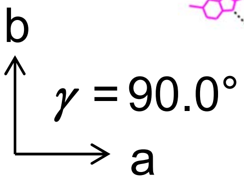
$p12_11$ (#9), z'=1
(if layer buckling is ignored)

Overlay by translation of all five layers (001) after rotation by 180° of the B layers





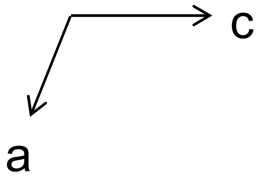


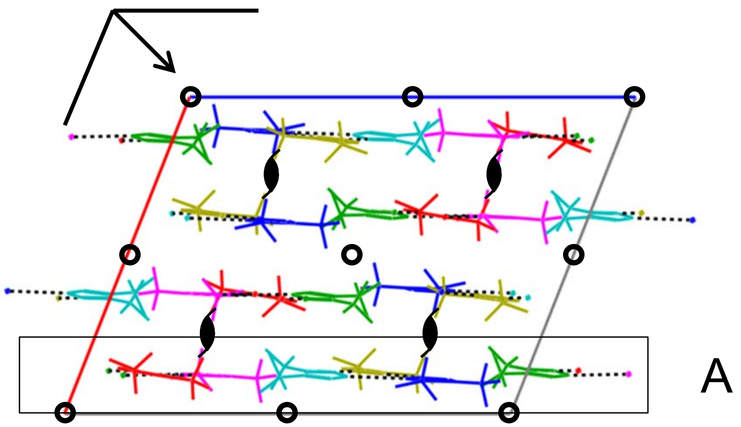


an A layer
(A1)

a B layer
(B1)

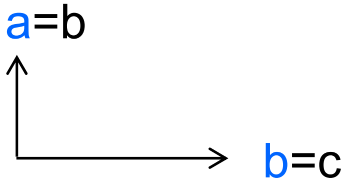
Projection along **b**

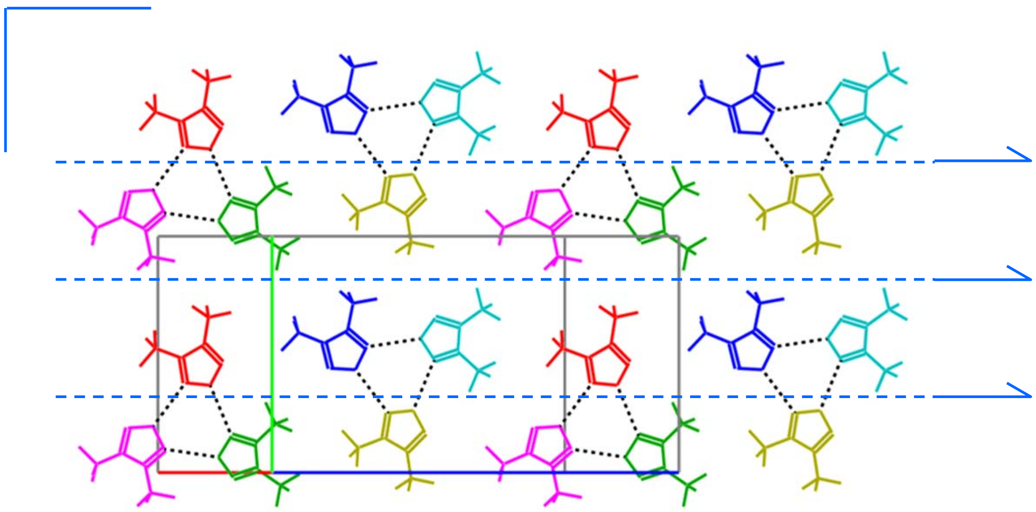




DATTAV
($P2_1/n$, $Z'=6$)

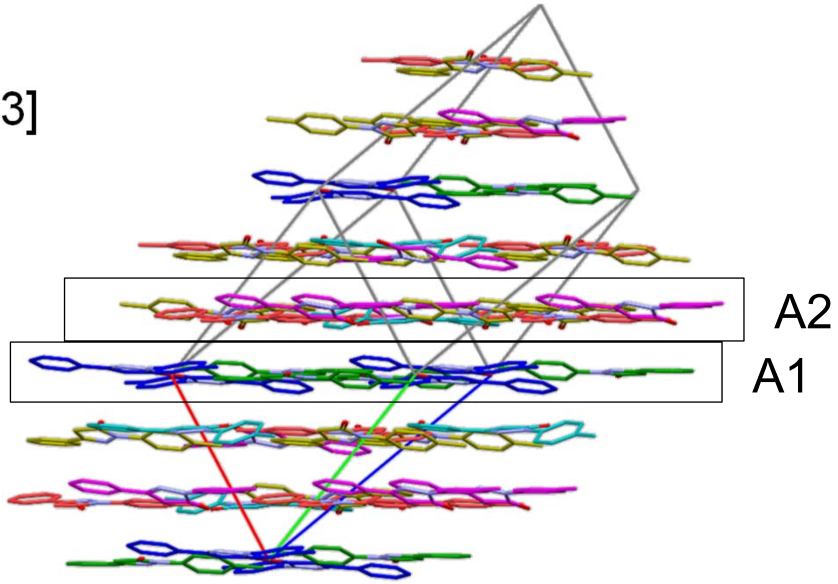
Layer (100)





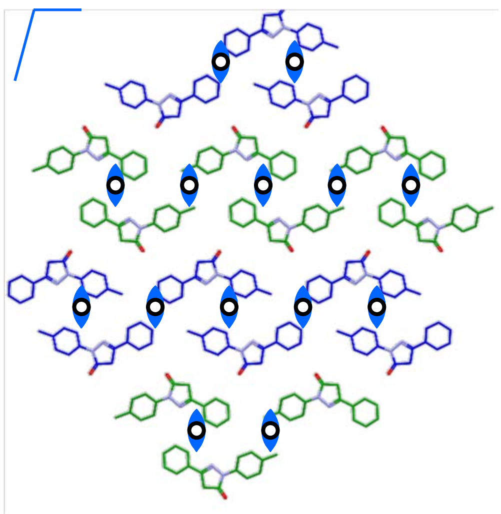
$pb2_1m$ (#29),
$z'=3$

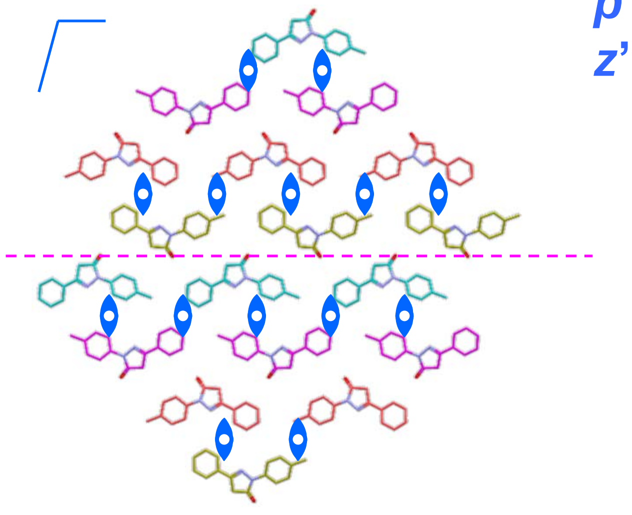
Projection along [1$\bar{4}$3]



DEZQUW
($P\bar{1}$, Z'=6)

Layers [111] A1 and A2

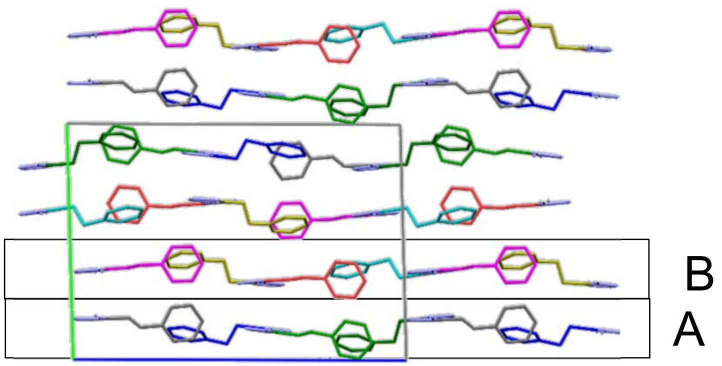




***p*112/*m* (#6),**
***z*'=2**

(There are local glides/ screws but they can only be local because the axes for translation are not mutually perpendicular.)

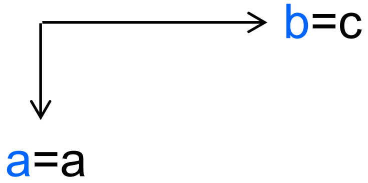
Projection along **a**



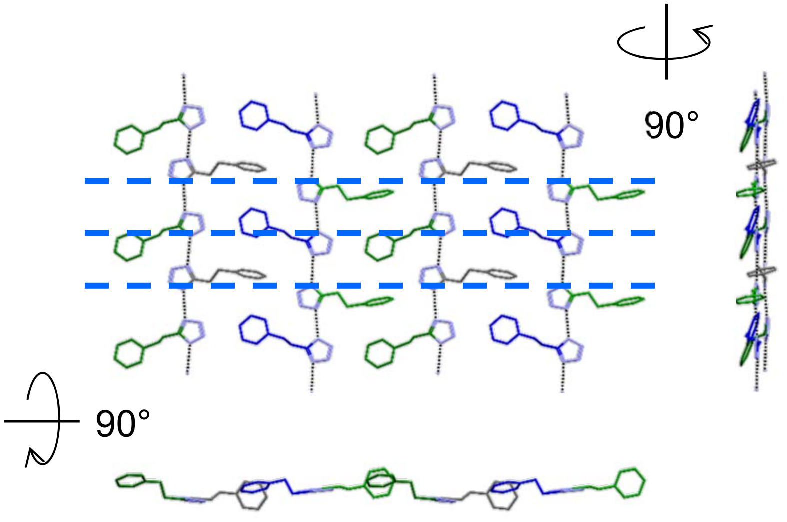
ELAJEI
($P\bar{1}$, Z'=8)

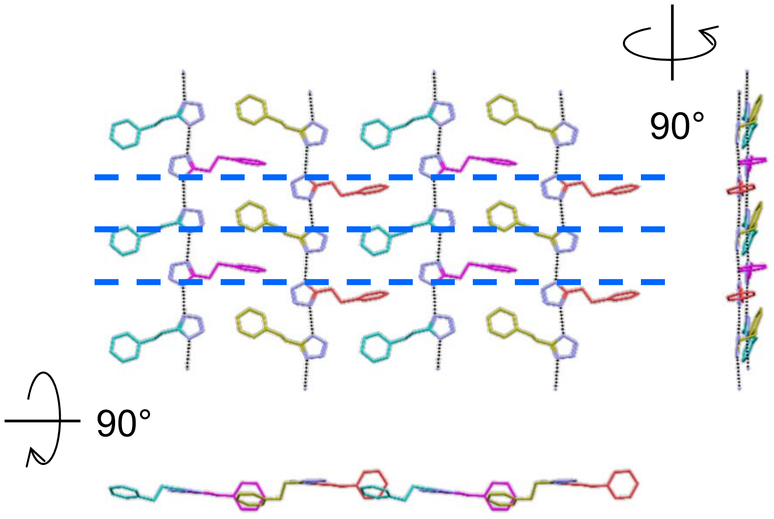
Layers (010) A and B

A and B are related by an approximate local glide with mirror perpendicular to b with a translation of about a/3 (α = 91.7°)



***pb*11 (#12), *z'*=2**

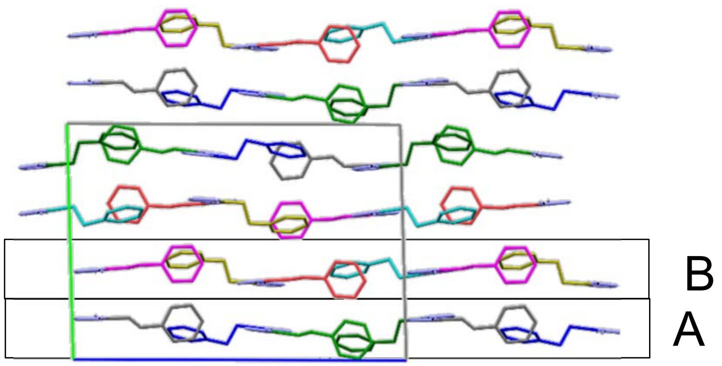




(see also next page)

ELAJEI,
con't
($P\bar{1}$, Z'=8)

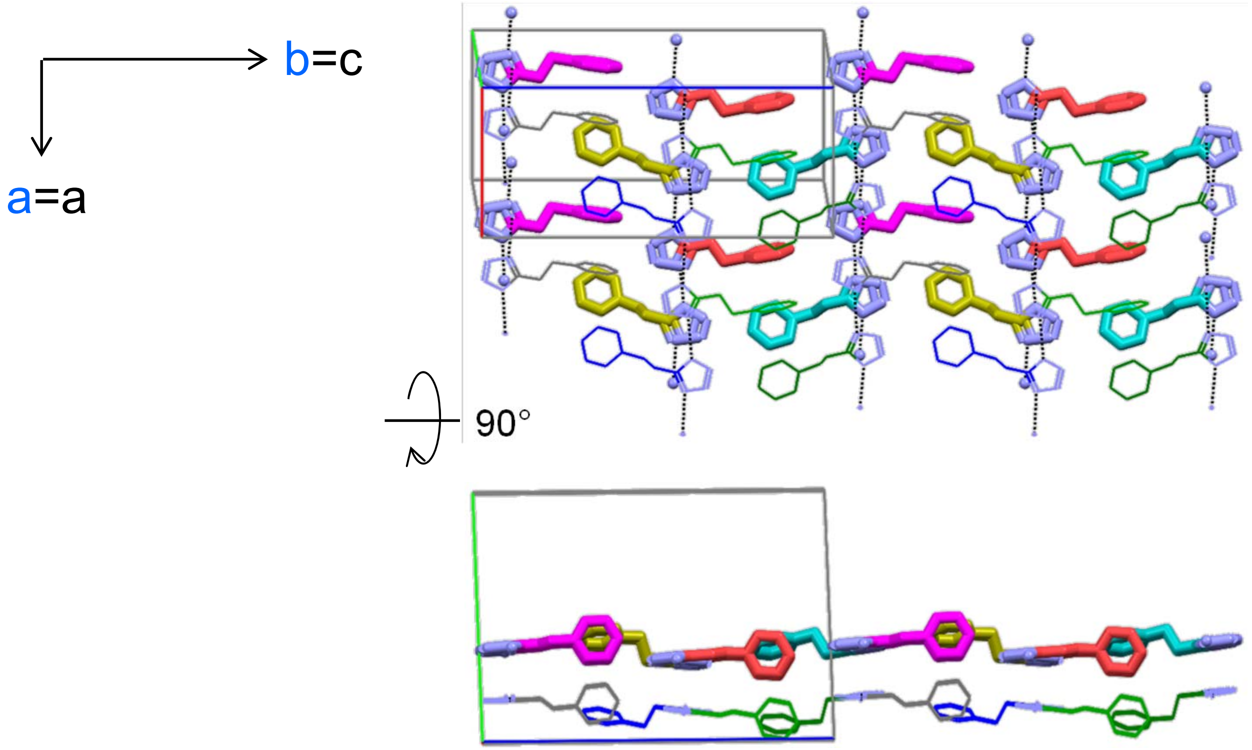
Projection along **a**



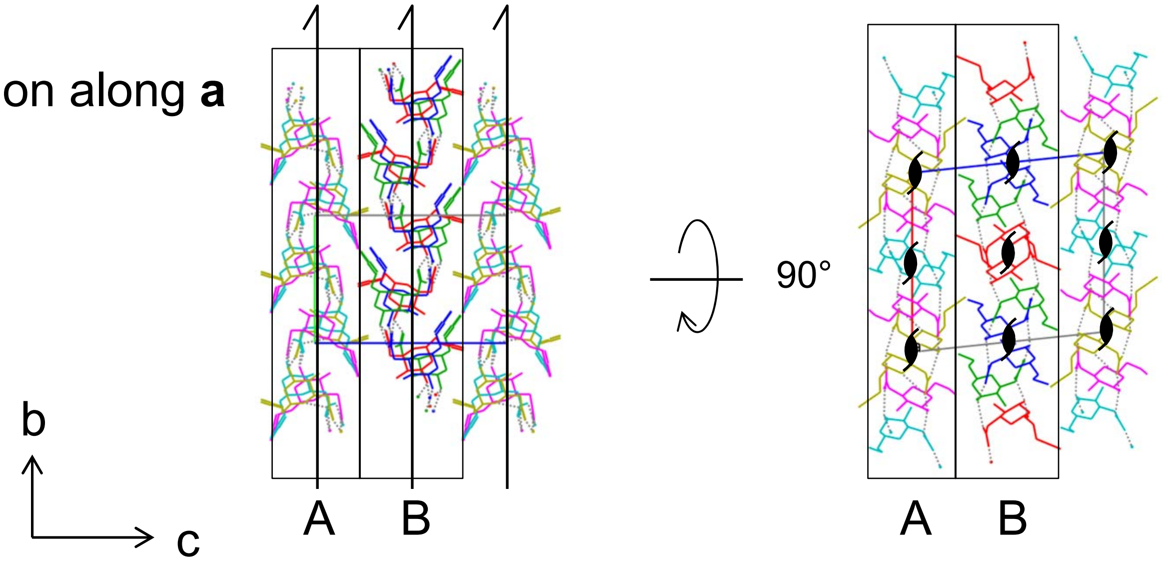
Layers (010) A and B in projection along **a***

A and B are related by an approximate local glide with mirror perpendicular to b with a translation of about a/3 (α = 91.7°)

***pb*11 (#12), *z'*=2**



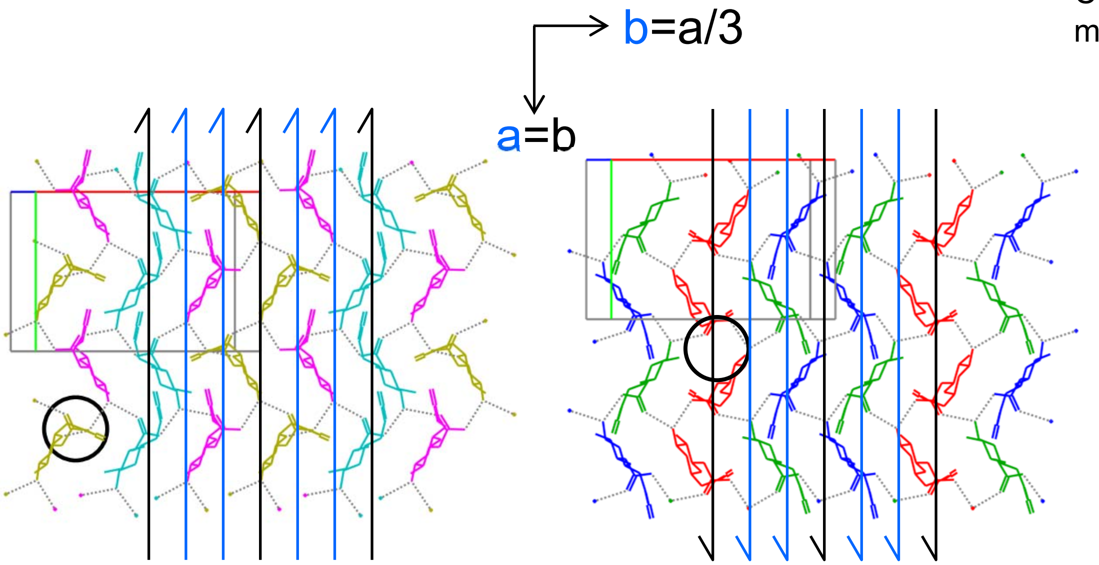
Projection along **a**



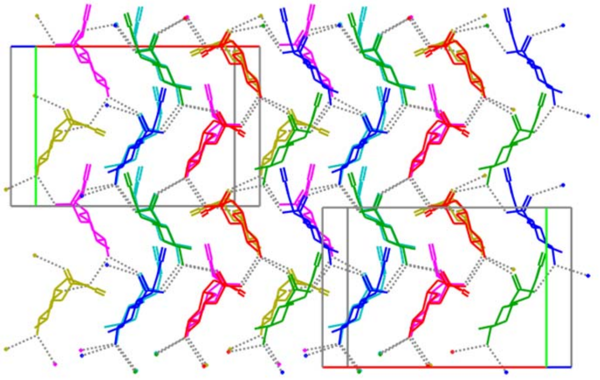
FADQAF
($P2_1$, Z'=6)

Layers (001): A, B and their best superposition after rotation of layer B by 180° around **c***

[the **a**/3 pseudotranslation and the two approximate 2_1 axes (especially in the A layer) are degraded by the conformations of the $CH_2C=C=CH_2$ groups, especially the groups of molecules #3 and #4]



$p2_111$ (#9), z'=1 (1/3rd of 2_1 axes exact)

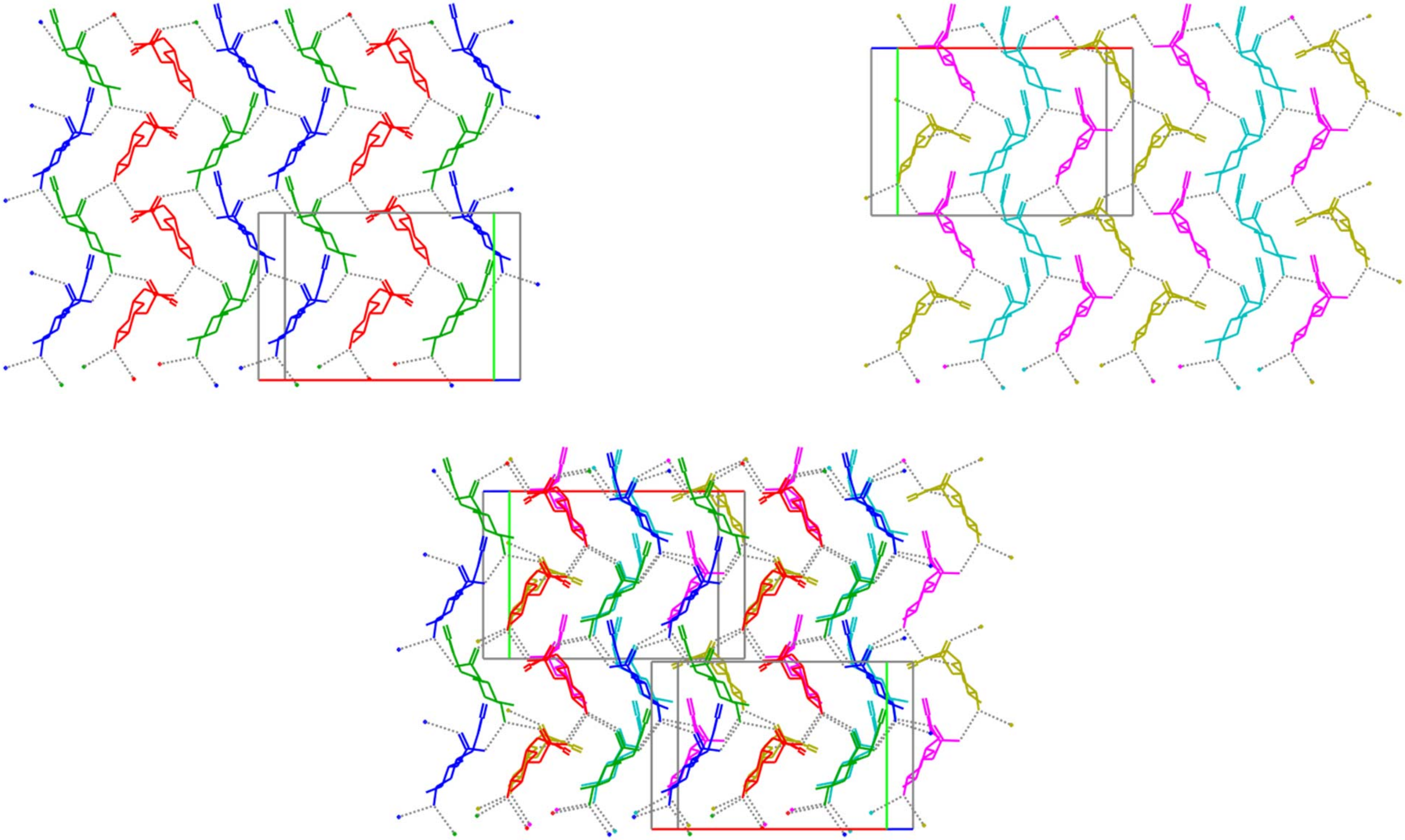


Superposition does not always line up the same molecules (*e.g.*, #2&5 and #2&6) so the relationship between the layers cannot indicate pseudosymmetry

(see also next page)

Layers (001): Larger view of A, B and their best superposition after rotation of layer B by 180° around **c*** and translation (the orientations of the buta-2,3-dienyl groups make the rotation necessary)

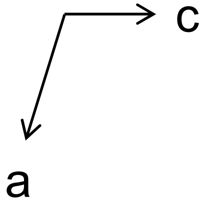
FADQAF
con't
($P2_1$, Z'=6)

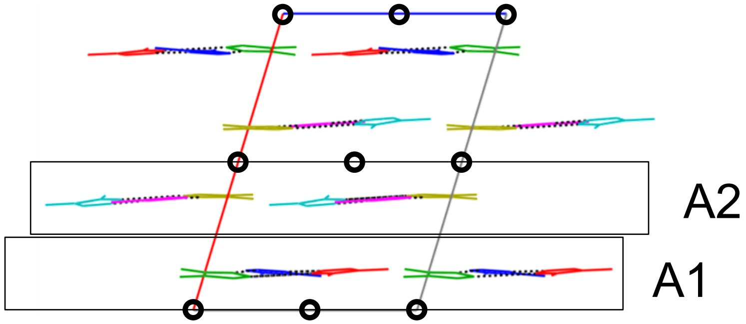


Projection along **b**

FITQAA

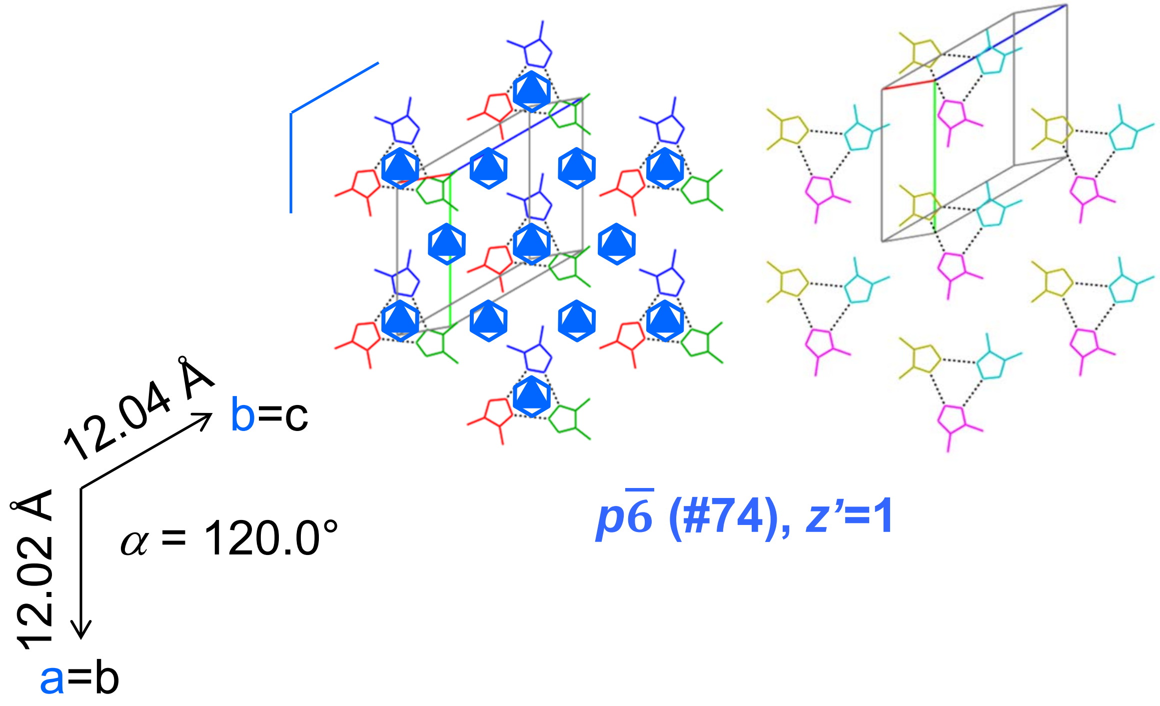
($P\bar{1}$, Z'=6)



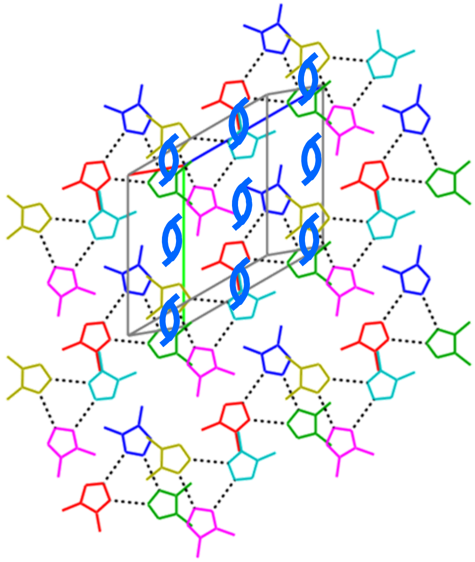


Layers (100): A1 and A2

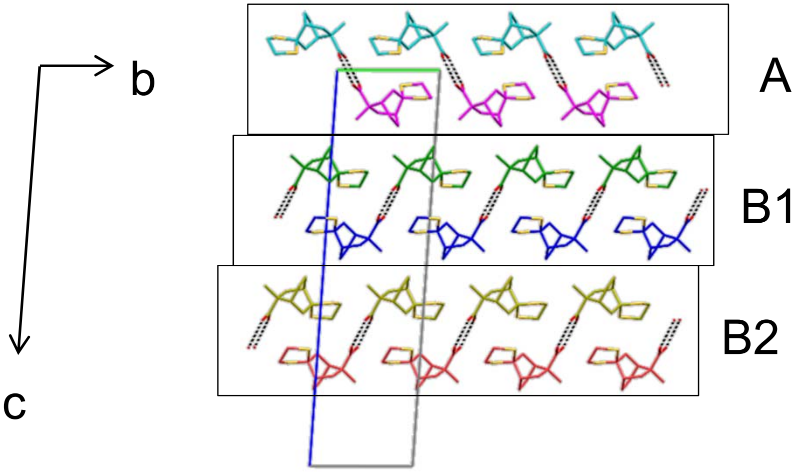
Two-layer slab (100), $0 < x < ½$ with layers related by approximate, local 2_1 axes



$p\bar{6}$* (#74), *z'=1



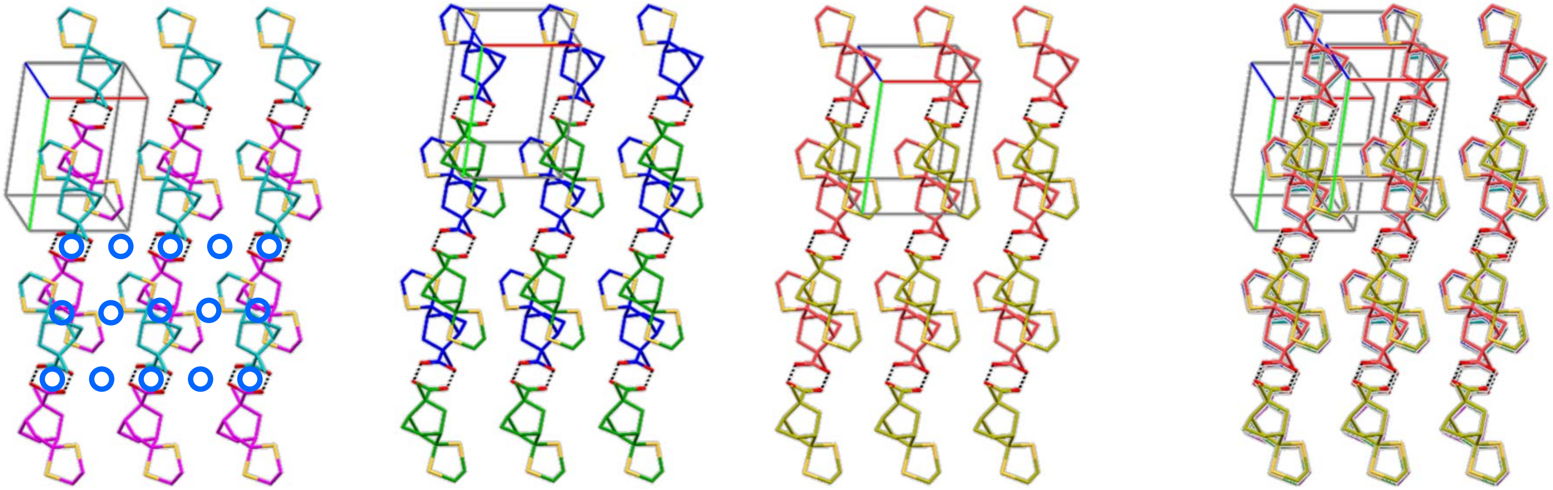
Projection along **a**



GIPLID
(*P*1, *Z*'=6)

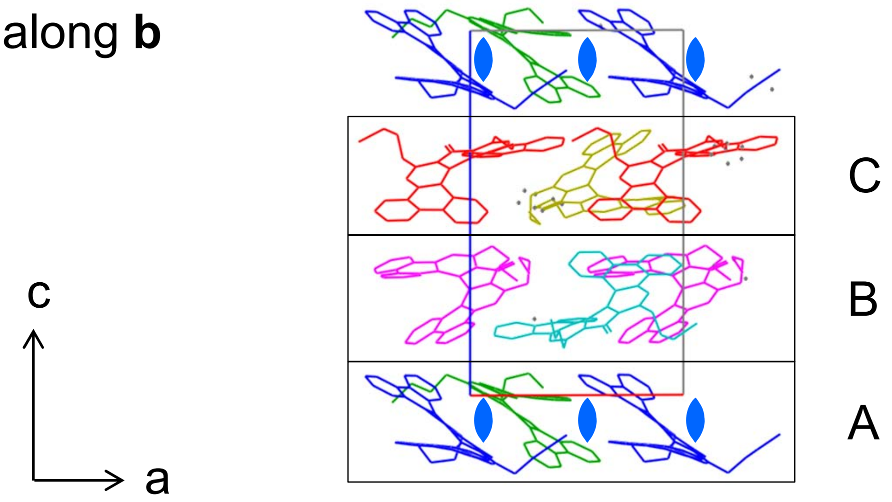
A, B1, and B2 are the same in projection but the dimers in A have a different orientation

Layers (001) in projection: A, B1, B2 and their superposition with translation



$p\bar{1}$ (#2), z'=1

Projection along **b**



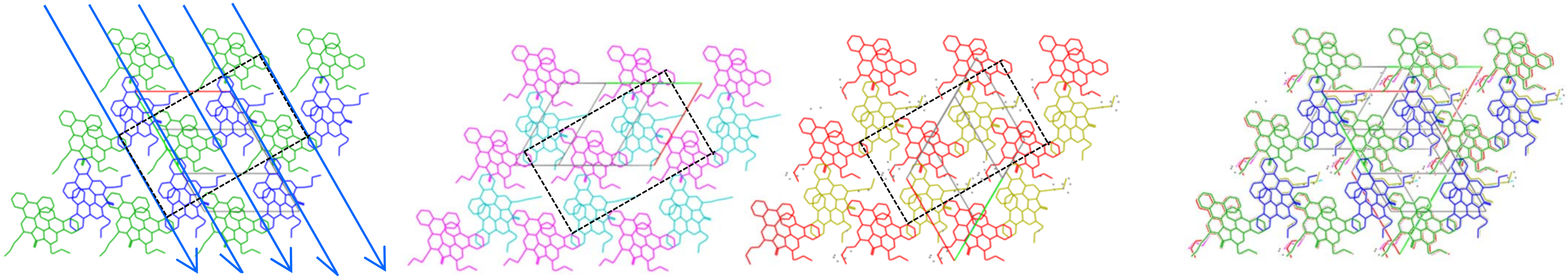
HASYUX
(*P*1, *Z*'=6)

Cell constants:
15.34, 15.37. 23.88 Å
72.5, 81.2, 60.2°

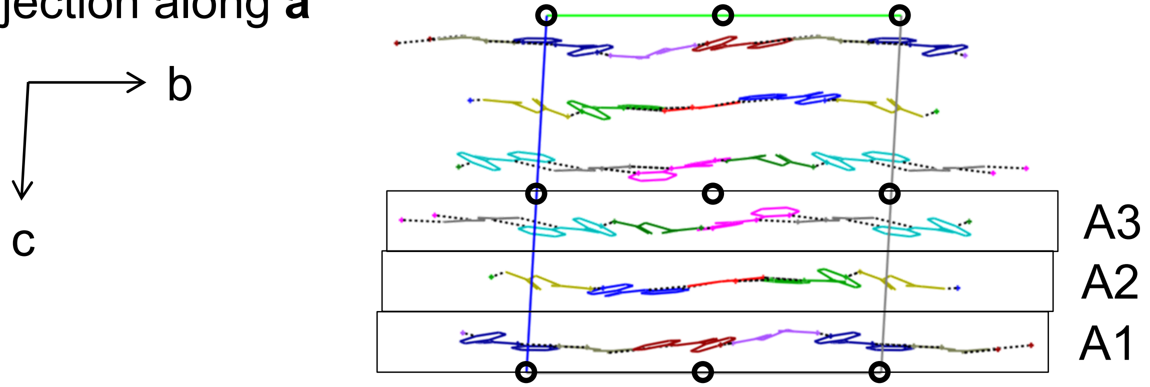
(pseudo 2s and 2_1s in other layers are not shown; they are rotated around the vertical by ± 120°)

Layers (001): A, B (rotated by +120°) and C (rotated by -120°)
After the rotation the layers can be superimposed well by translation except for one of the two sets of $(CH_2)_3Cl$ groups.

***c*211 (#10), *z*'=1** (cell shown in black; angle is 90.2°)

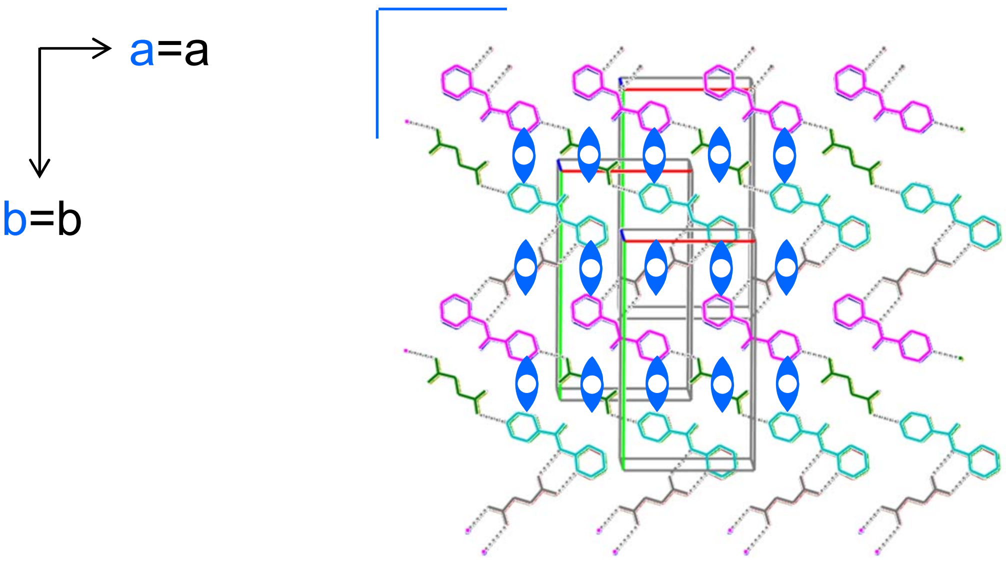


Projection along **a**



KAYGUO
($P\bar{1}$, Z'=6)

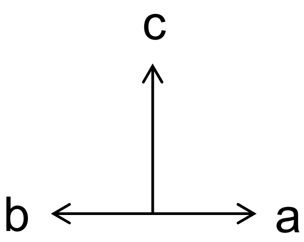
Superposition by translation of layers (0 0 1): A1, A2 and A3
(layers are related by [3 -2 1]/6)

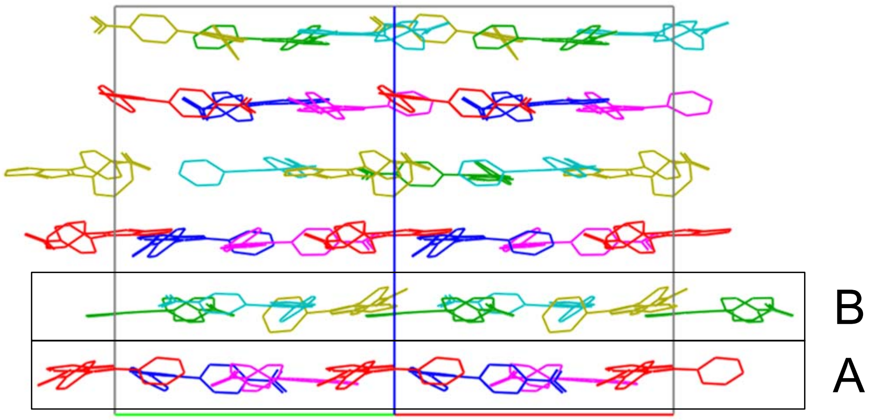


***p112/m* (#6),**
***z'*=1**

Projection along **c**

KOFTEG
($P3_2$, $Z'=6$)

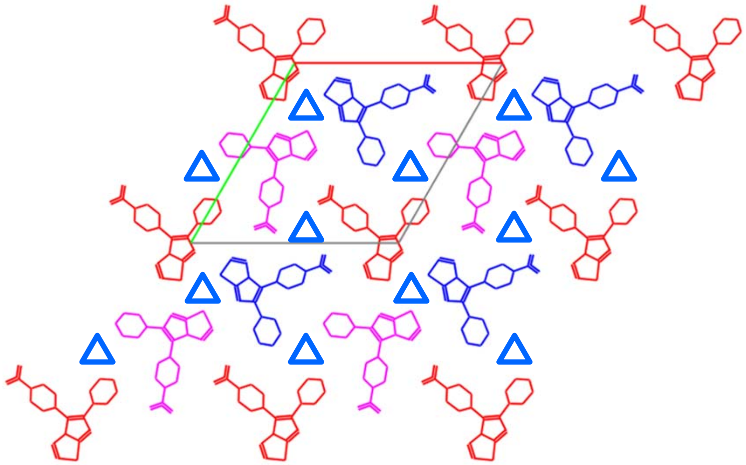


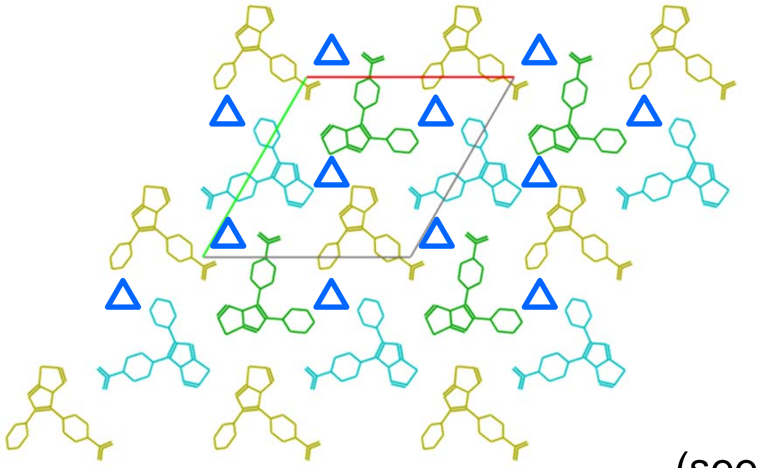


Layers (001): A and B

***p*3 (#65), *z'*=1**

(threefolds are quite approximate because the molecules #2, 3 & 6 are the conformational enantiomers of molecules #1, 4 & 5; each layer contains two of one and one of the other)

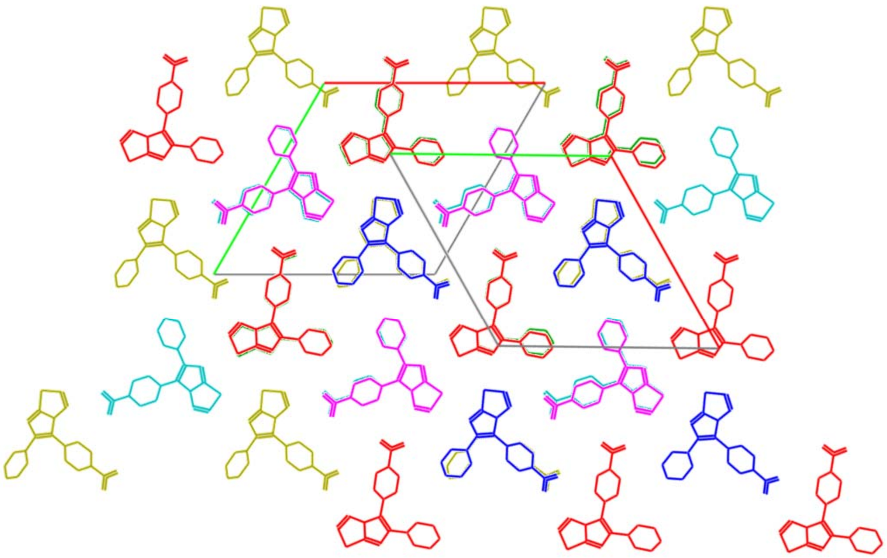




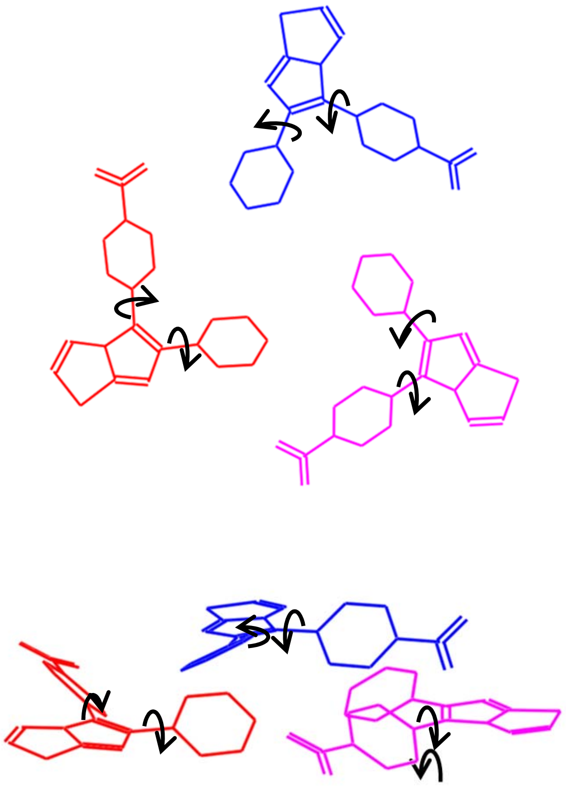
(see also next page)

Overlay of layers (001) A (at z = 0.09) and B (at *z* = 0.26; Δ*z ca* 1/6) after rotating layer A

KOFTEG,
con't
($P3_2$, Z'=6)



Molecule #5 is the conformational enantiomer of molecules #2 & 3

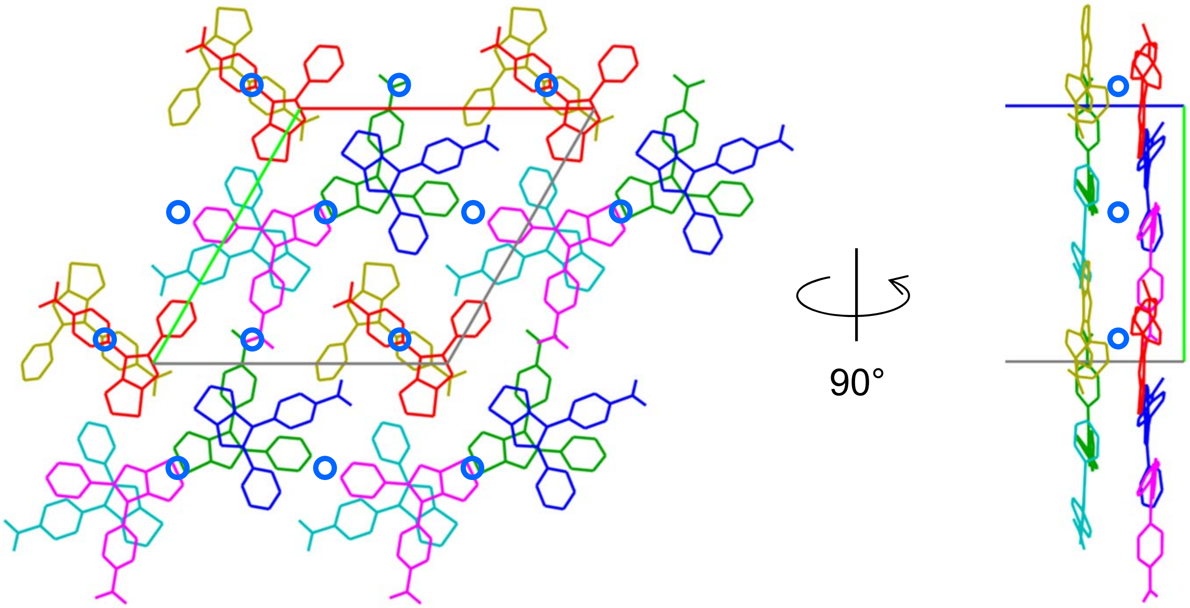


(absolute values for torsion angles for Ph and O_2N-Ph are 24-42°; averages are 31.5° for Ph and 35.2° for O_2N-Ph)

(see also next page)

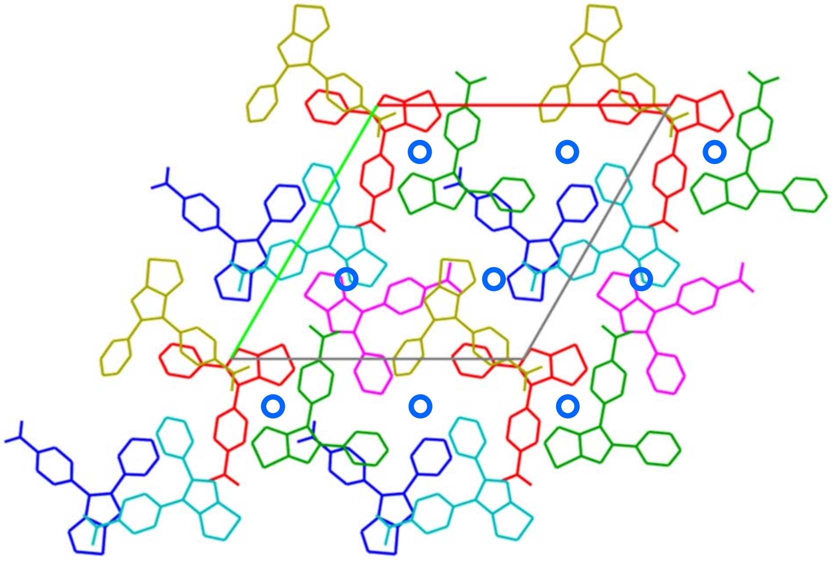
KOFTEG, yet again ($P3_2$, $Z'=6$)

Layers (001): A and B



Approximate local inversion centers relate conformational enantiomers #3 and #4 but also relate molecules #1 & #5. as well as #2 & #6 that have the same conformation

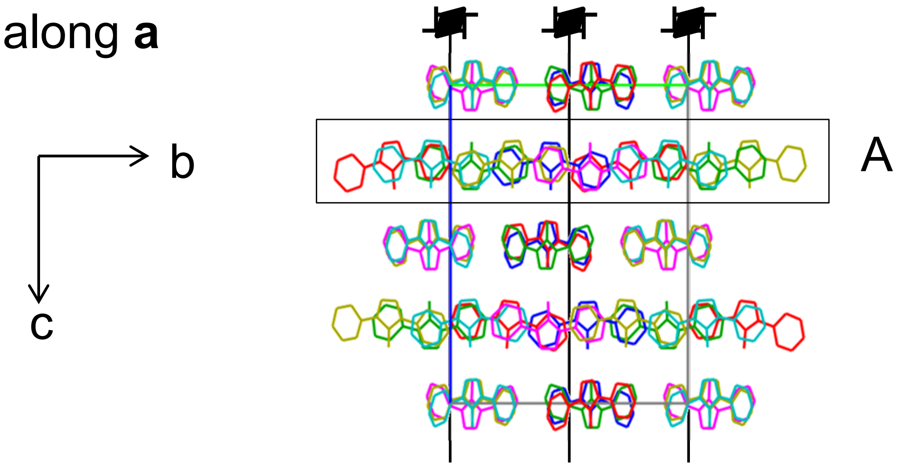
Layers (001): B at z = 0.26 and A' at z = 0.43



Approximate local inversion centers between these two layers do relate conformational enantiomers

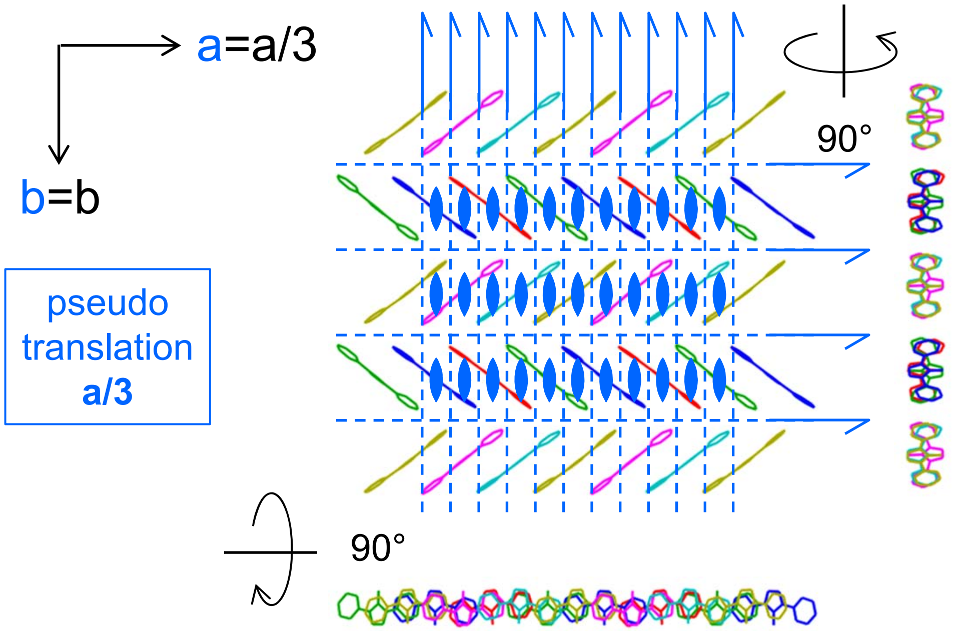
Projection along **a**

LADQAL
($P4_1$, Z'=6)



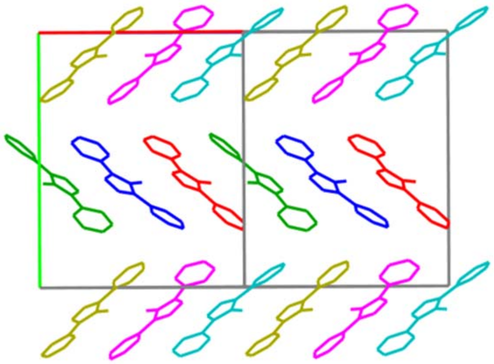
Layer (001) near z=0

$p2_12_12$ (#21) or $pba2$ (#25), z'=½

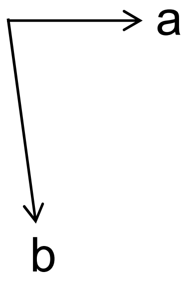


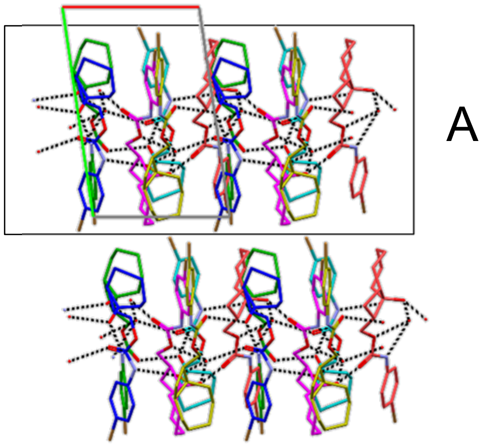
pseudo
translation
a/3

View along [10$\bar{1}$] of
the layer to show the
alternation pattern



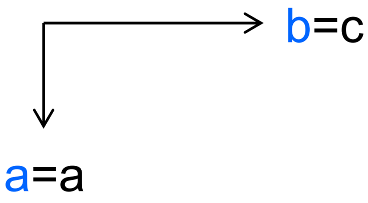
Projection along **c**

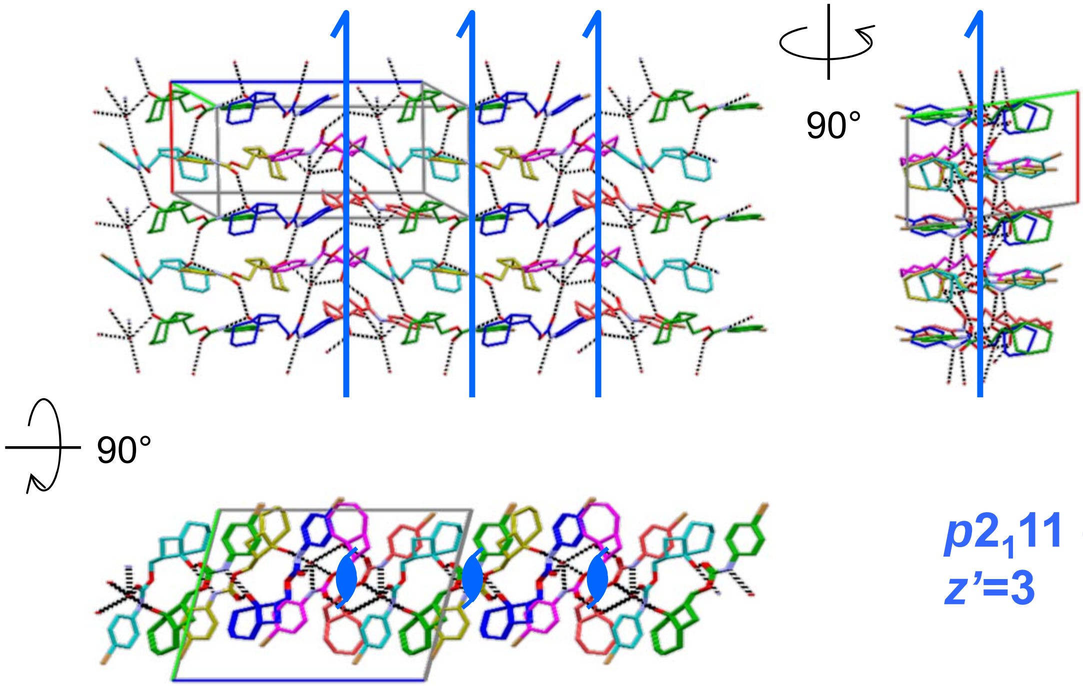




LITNIM
(*P*1, *Z*'=6)

Layer (001): A

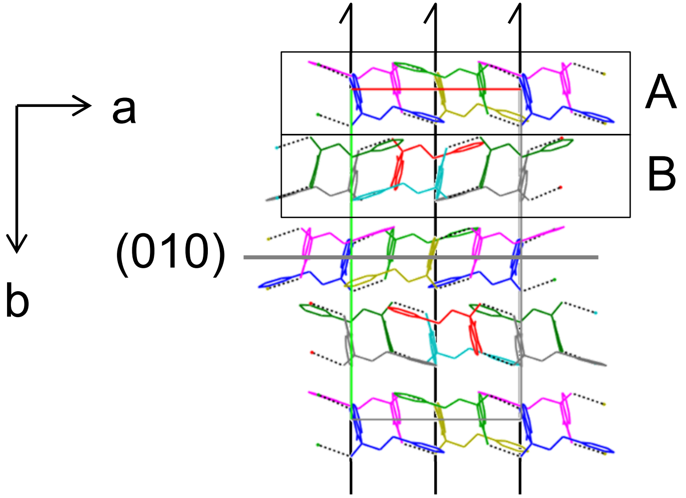


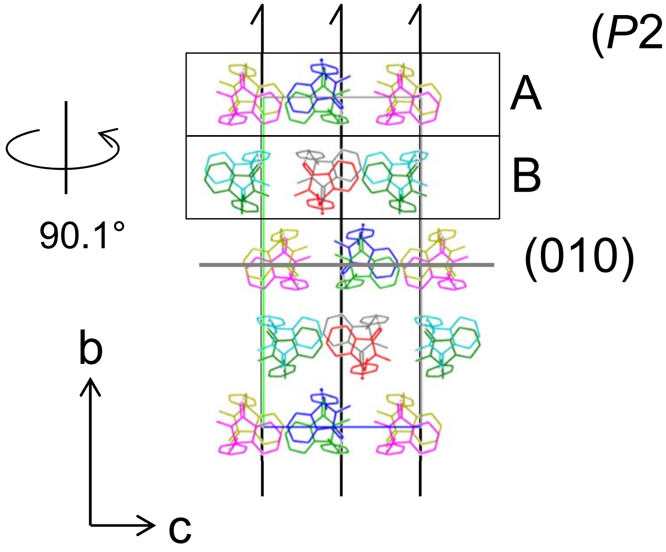


***$p2_111$* (#9),**
***z'*=3**

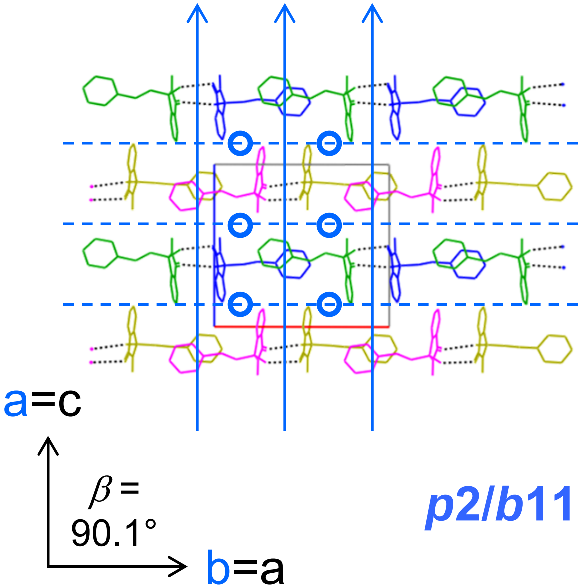
LUMJUZ
($P2_1$, Z'=8)

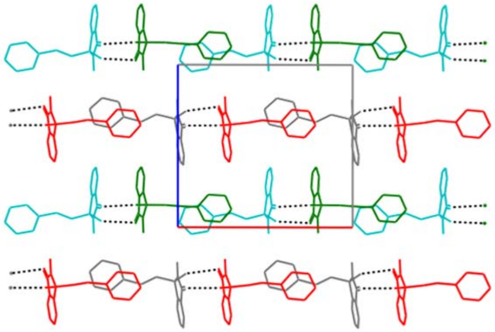
Projection along **c**





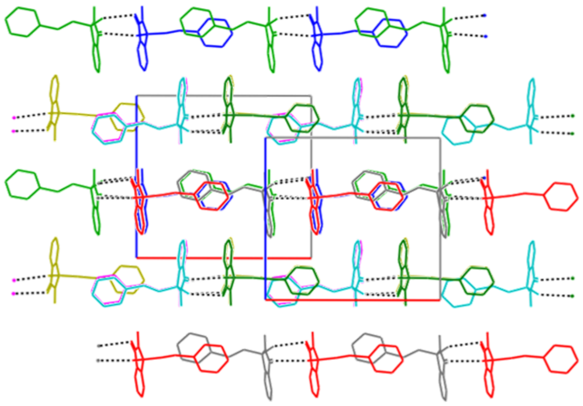
Layers (010) A and B





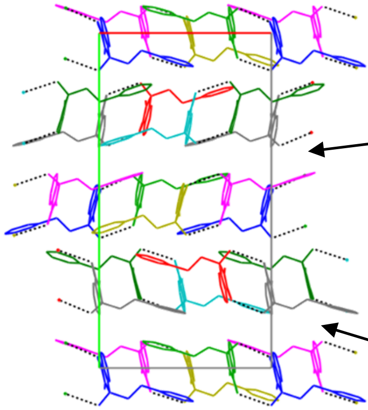
***p2/b11* (#16), *z'*=1**

Superposition of the two layers by translation *but* superposed molecules (#1,7; #2,3; #4,8; #5,6) are enantiomers



Superposition by translation is possible if one of the layers is rotated by 180° around its normal

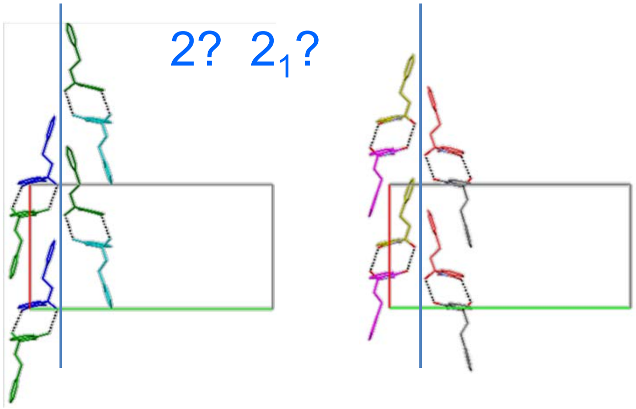
LUMJUZ,
con't
($P2_1$, Z'=8)



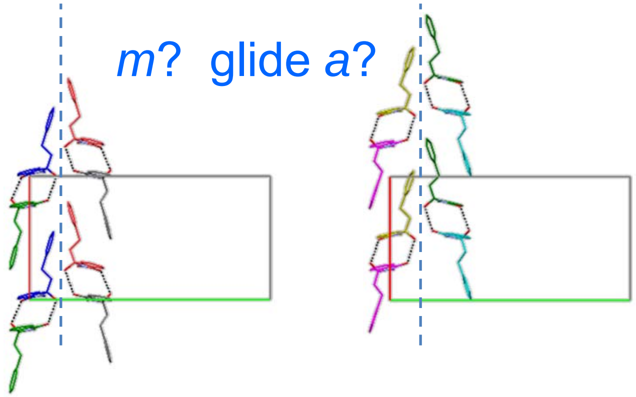
No 2_1 axis or glide is possible between layers because there is enantiomeric alternation on both sides of the layer interface

It is not clear (see below) how the relationship between the layers should be described

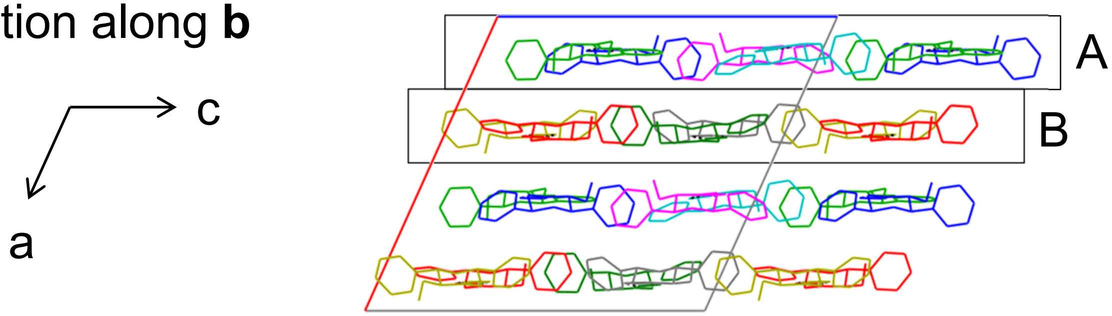
All molecules homochiral



Molecules in dimers are
homochiral;
Molecules in different dimers
are heterochiral



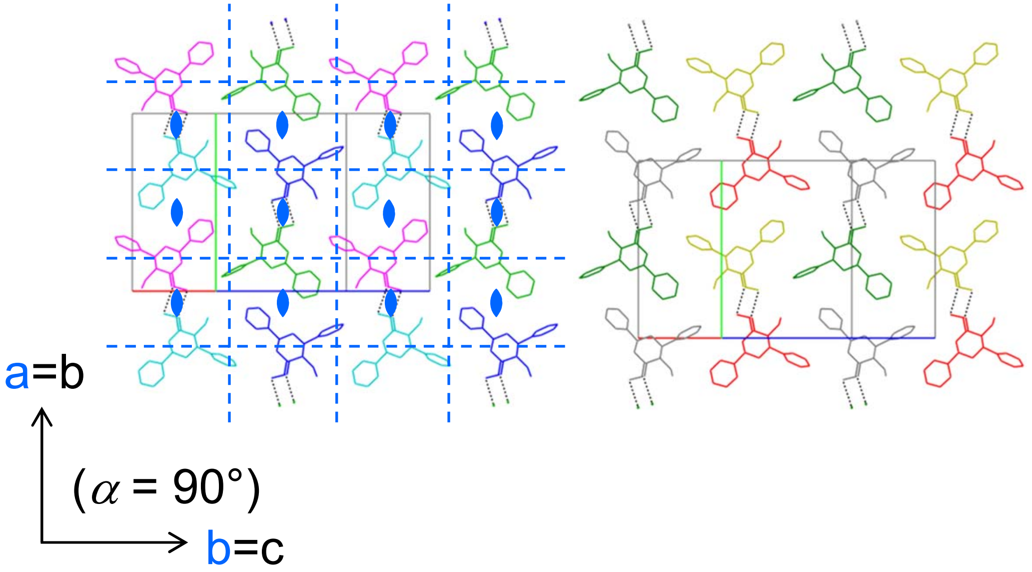
Projection along **b**



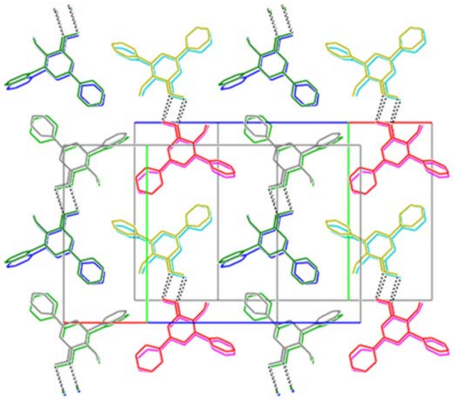
LUMYAT
(*Pa*, *Z*'=8)

Layers (100) A and B

***pba*2 (#25), *z'*=1**

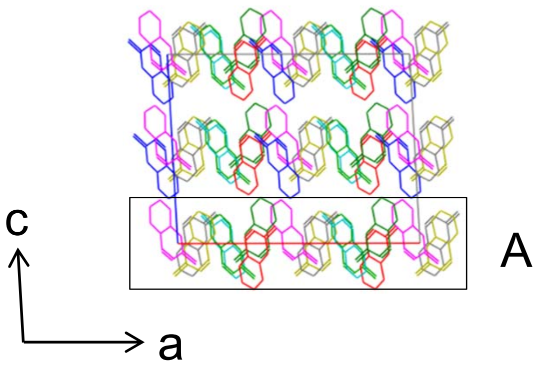


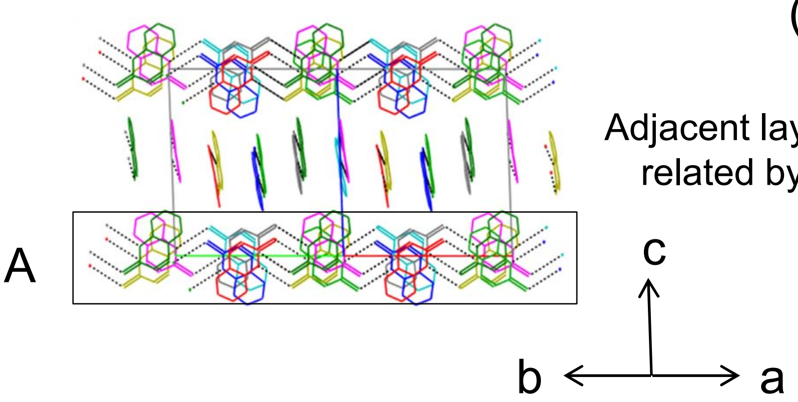
Superposition of the layers by
inversion and translation



Projections along **b** and along [101]

MAJSOG
(*Cc*, *Z*'=8)

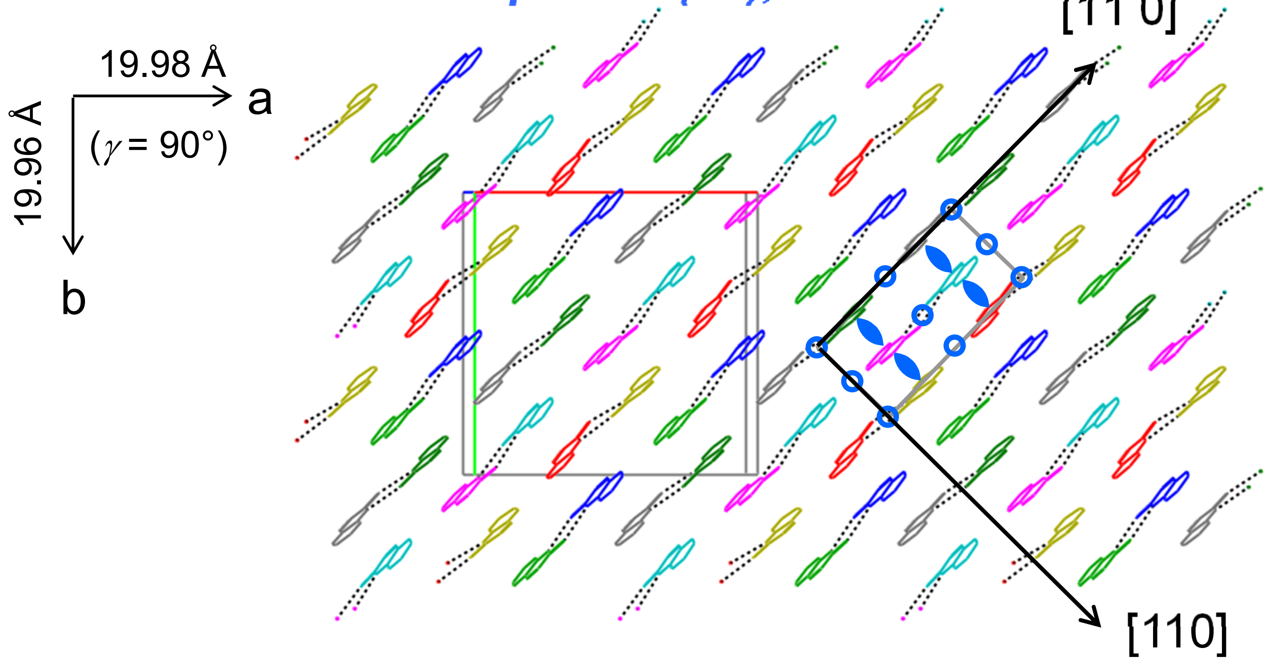


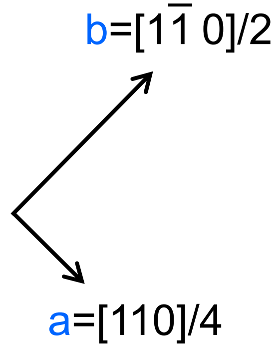


Adjacent layers (001) are related by the *c* glide

Layer (001) at *y*=0

***p*112/*n* (#7), *z*'=1**



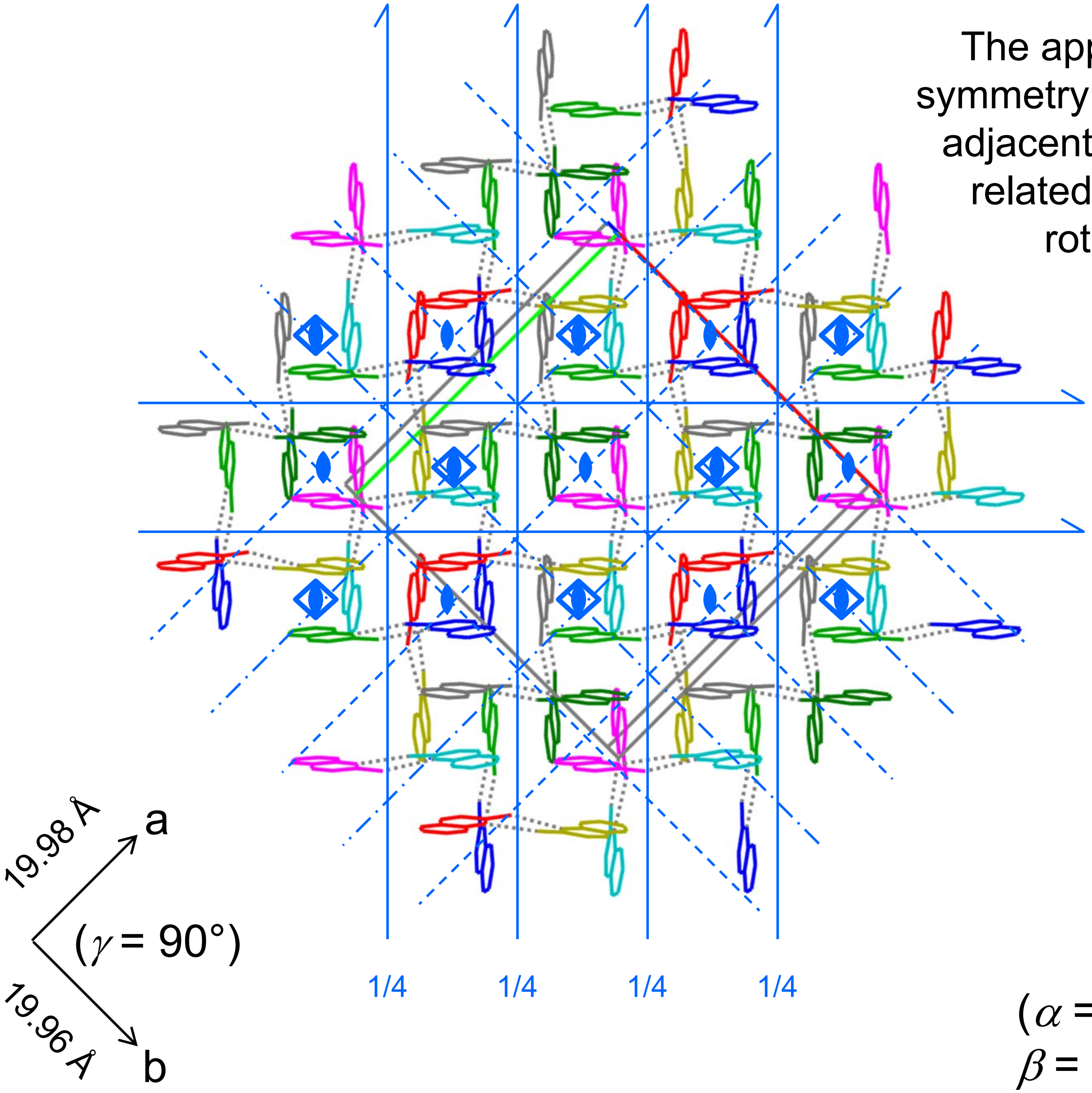


Pseudotranslation [110]/4 includes the *C* centering of the 3-D cell

(see also next page)

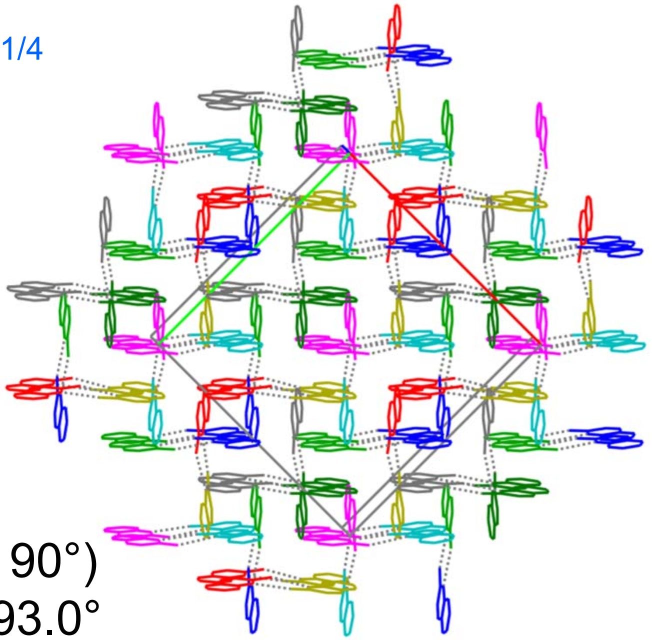
Projection along **c*** showing two adjacent layers (001)

MAJSOG,
con't
(*Cc*, *Z*'=8)



The approximate symmetry elements in adjacent layers are related by a 90° rotation

Projection along **c*** showing three layers

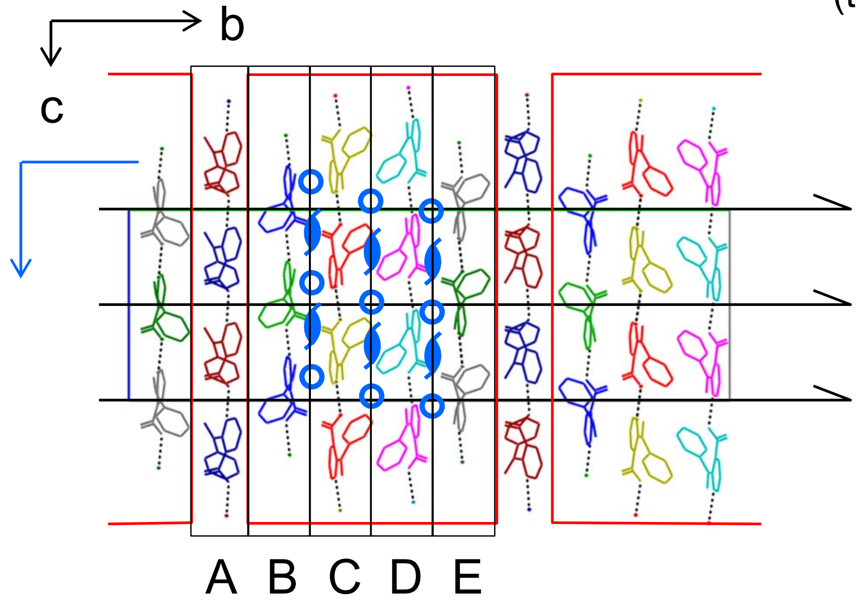


(α = 90°)
β = 93.0°

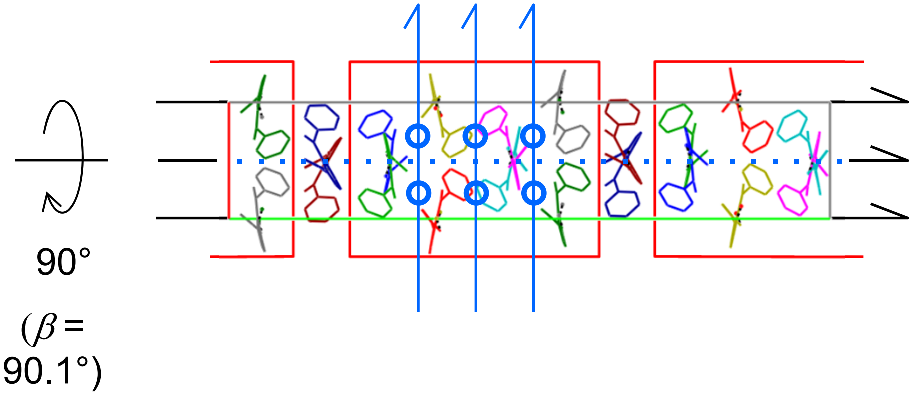
Projection along **a**

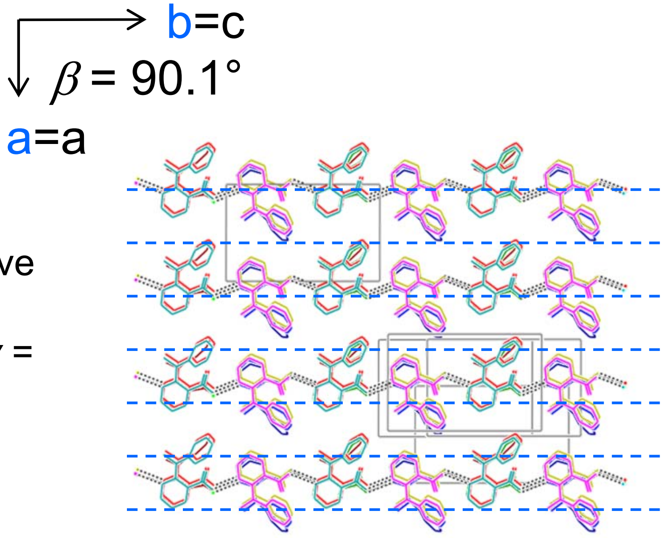
MOTNUF03
($P2_1$, Z'=10)

(the approximate 2_1 axes and $\bar{1}$ sites are local only)



Layers (010) A - E



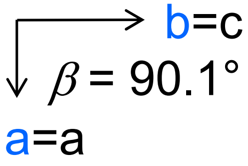


Overlay by translation of five independent layers (0 1 0) after inversion of layer at *y* = 0.35 (C) and layer at 0.55 (E)
[Layer at *y ca* 0.15 (A) is somewhat different in the third direction]

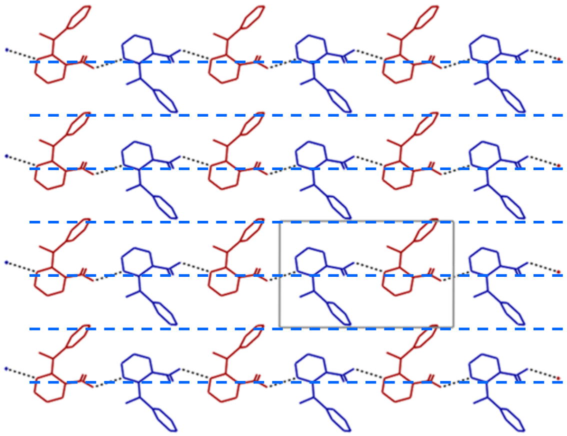
***pb*11 (#12), *z'*=1**

(see also next page)

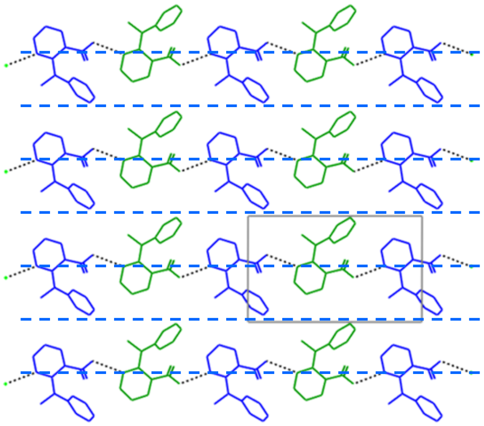
MOTNUF03
con’t
($P2_1$, Z'=10)



A; *y ca* 0.15 →

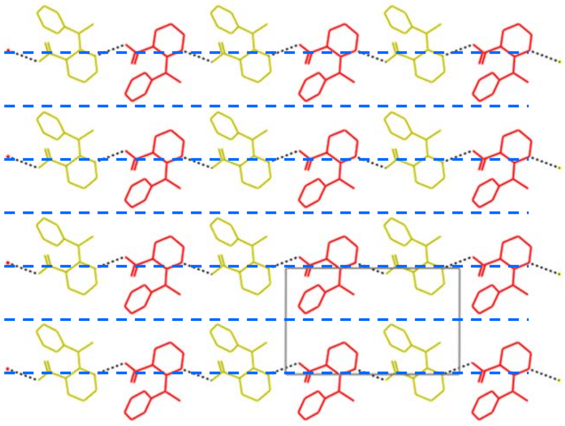


B; *y ca* 0.25 →

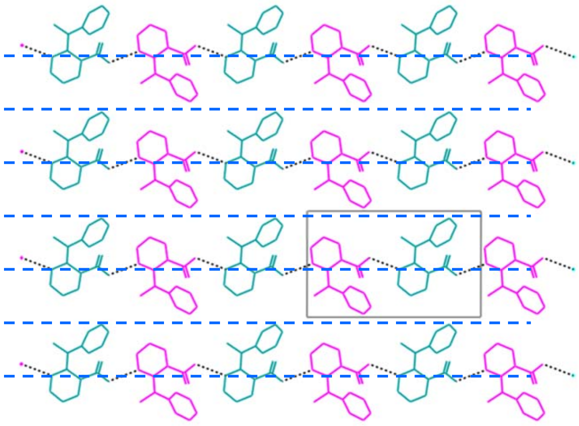


Layer projections can be superposed by translation if the layers at *y*=0.35 (C) and 0.55 (E) are inverted (arrows show direction of H-bonded chains) The layer at *y ca* 0.15 (A) is somewhat different in the third direction than the others.

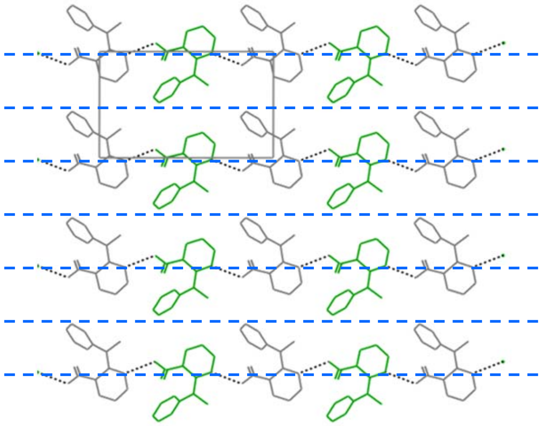
C; *y ca* 0.35 ←



D; *y ca* 0.45 →

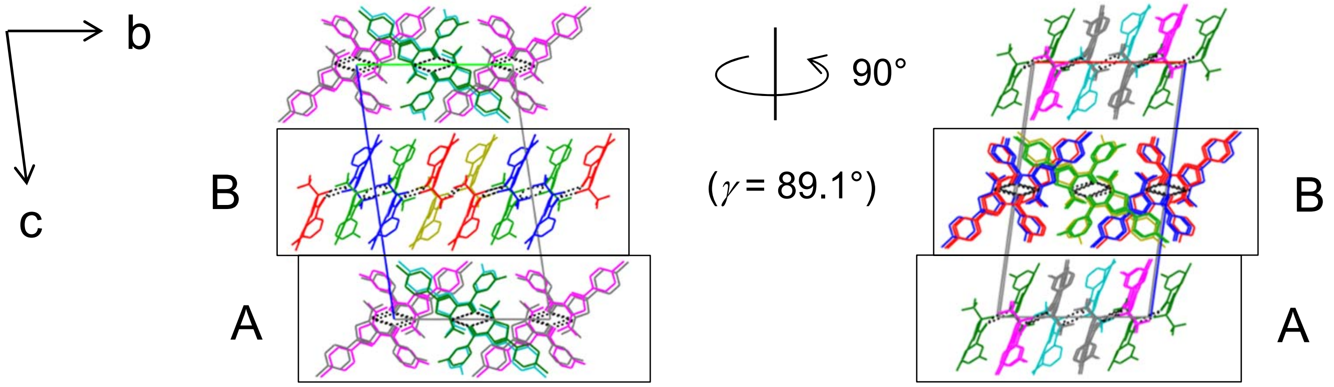


E; *y ca* 0.55 ←



Projection along **b**

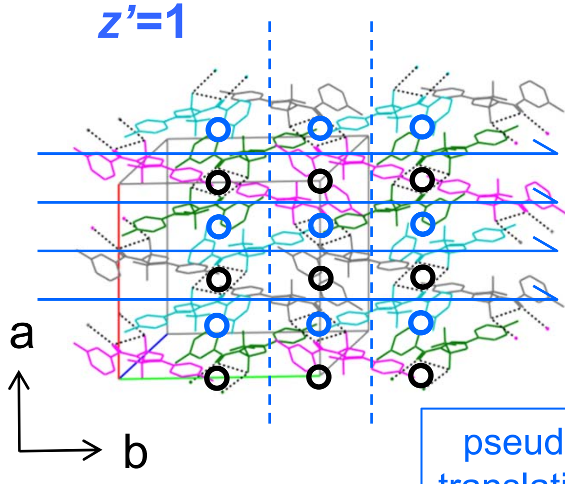
MUMHAE
($P\bar{1}$, Z'=8)



(γ = 89.1°)

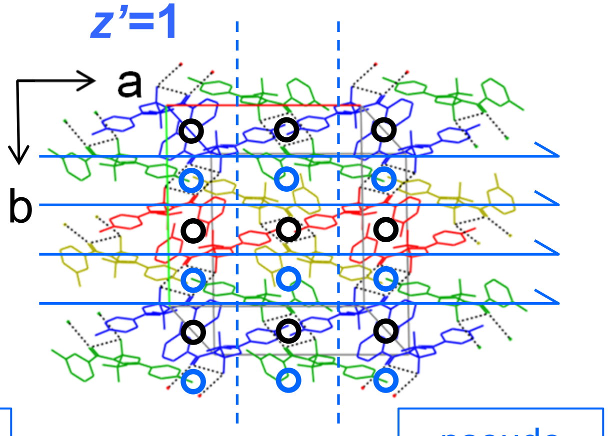
Layers (001): A and B (the latter rotated 90° around c*) and their superposition

$p12_1/a1$ (#17), z'=1



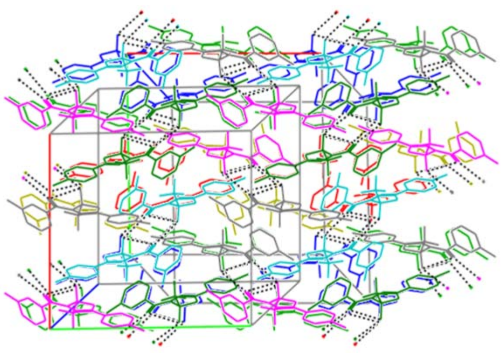
pseudo translation **a**/2

$p2_1/b11$ (#17), z'=1



pseudo translation **b**/2

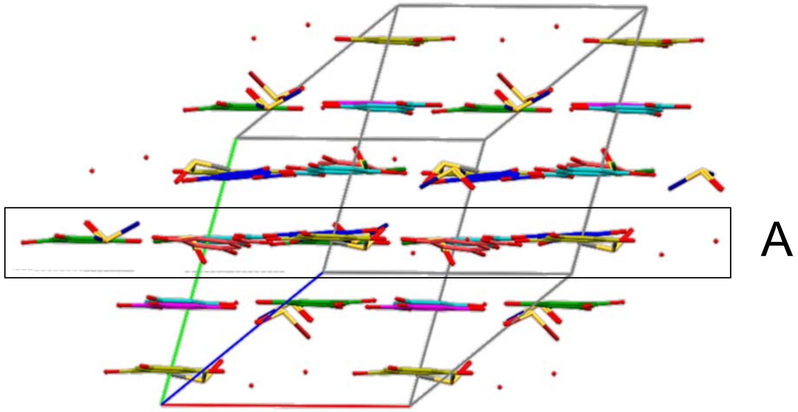
(a, b = 16.0, 16.5 Å; γ = 89.1°)



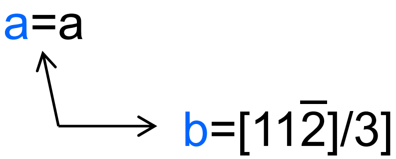
(α = 81.5°, β = 82.3° so layer offsets are large and the 4_2 axis is only local, see above)

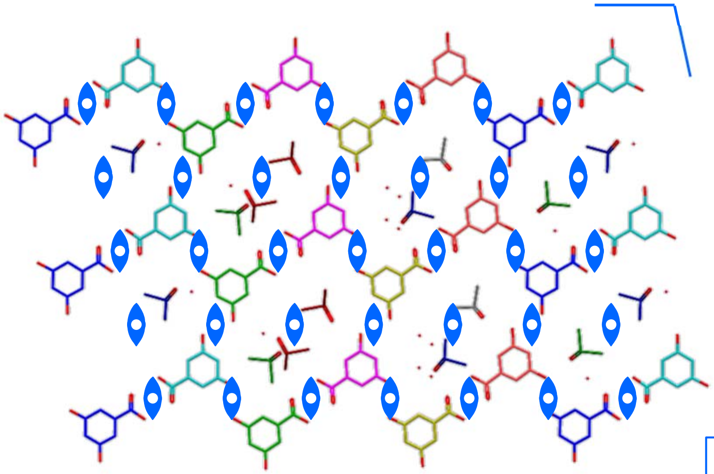
Projection along [$11\bar{2}$]

OKEJOE
($P\bar{1}$, Z'=6)



Layer (021)



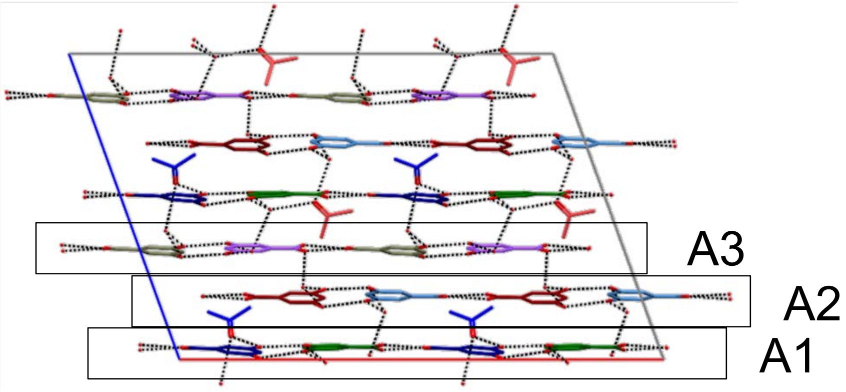


$p112/m$ (#6), z'=1
(host molecules only)

pseudo
translation
[$11\bar{2}$]/3

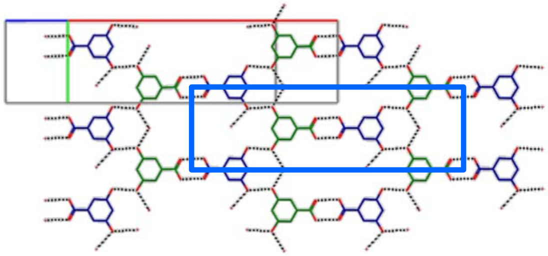
Projection along **a**

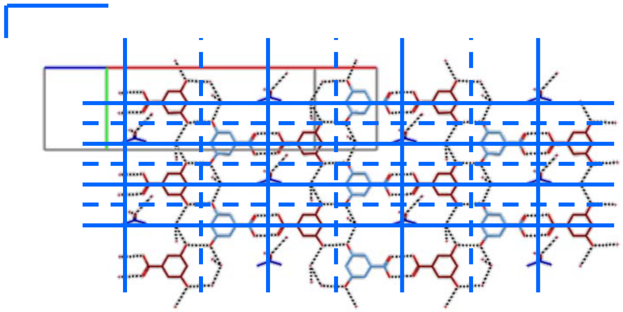
OKEKEV
(*Cc*, *Z*'=6)

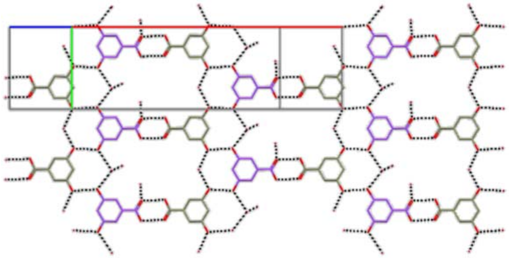


Layers (001) A1, A2, A3 and their superposition with translation

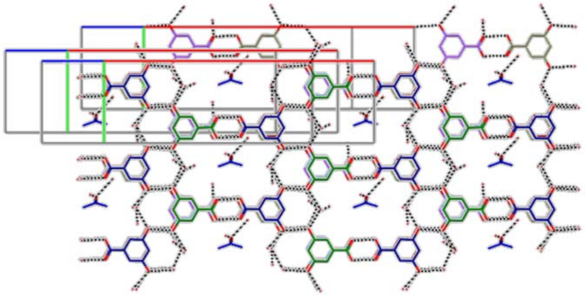
(inversion centers not shown;
rotation and screw axes not shown)



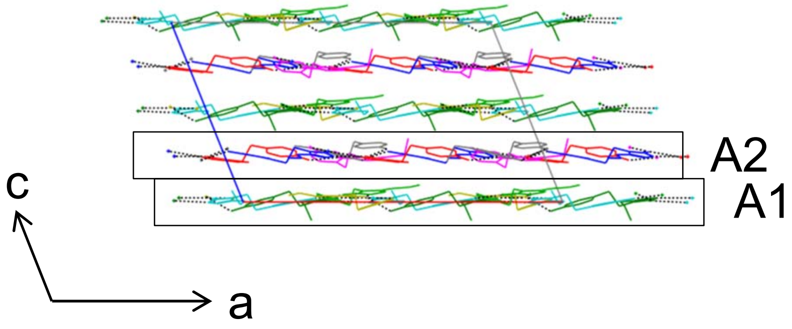




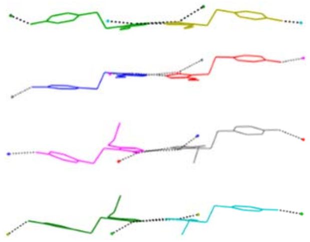
***cmmm* (#47), *z'*=1**
(host molecules only)



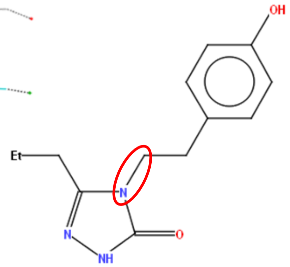
Projection along **b**



The four dimers



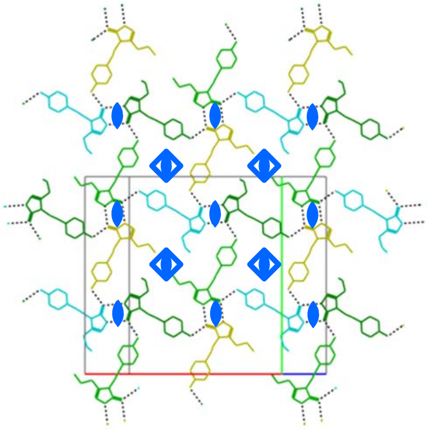
PAVLAB
(*Cc*, *Z*'=8)



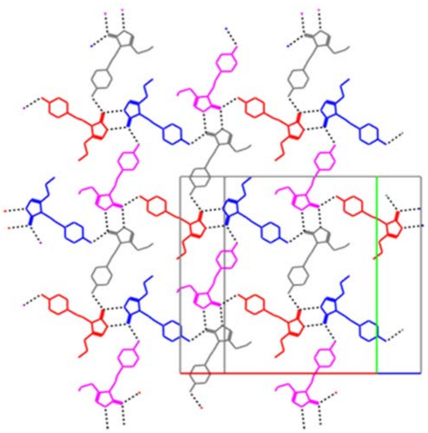
Pseudo-symmetry is imperfect because of different rotations around the marked N-C bond

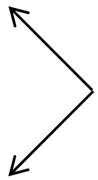
Layers (001) A1 ahd A2, and their superposition by translation

$p\bar{4}$ (#50), z'=1



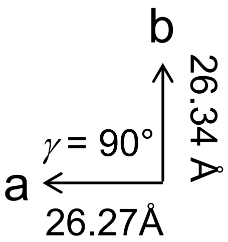
centering
(**a**+**b**)/2

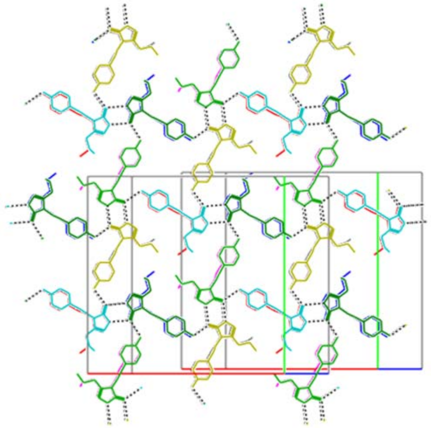




a=[110]/2

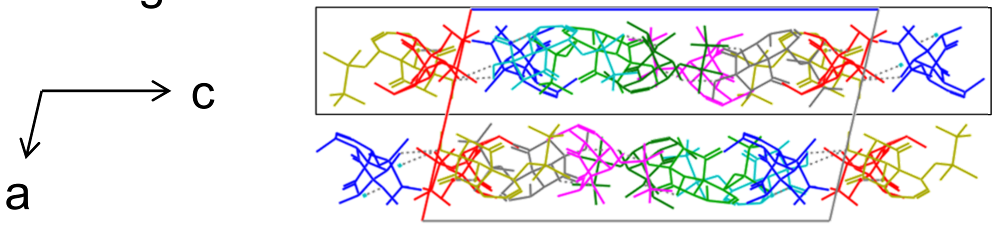
b=[1$\bar{1}$0]/2





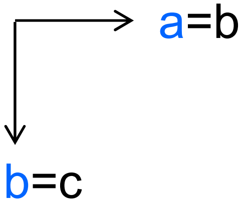
Projection along **b**

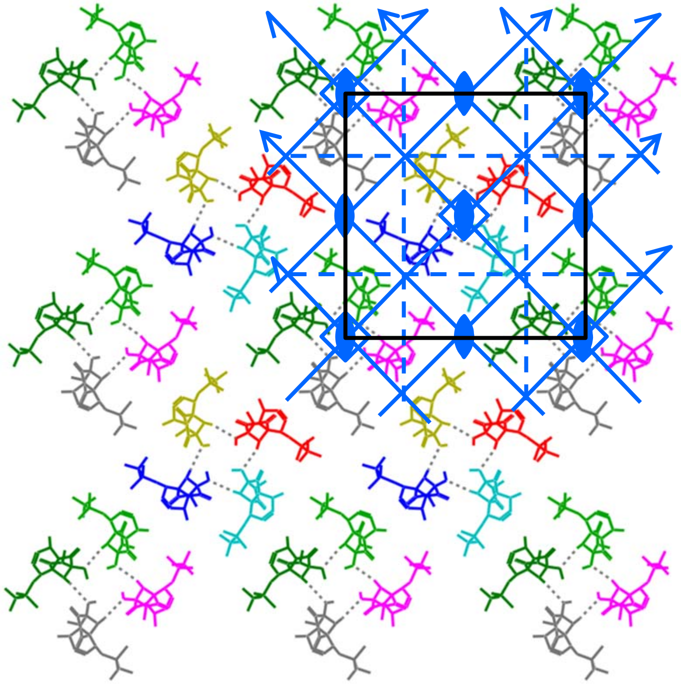
POVYEG
($P\bar{1}$, Z'=8)



A

Layer (100)

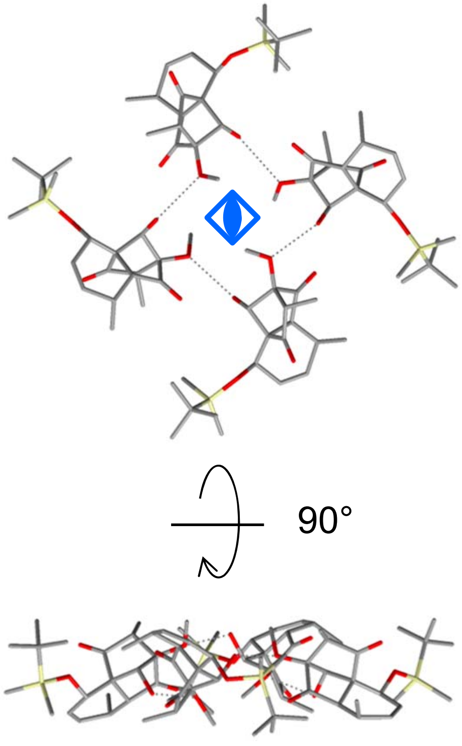




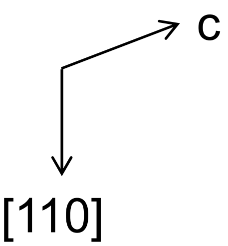
$p\bar{4}b2$ (#60),
***z'*=1**

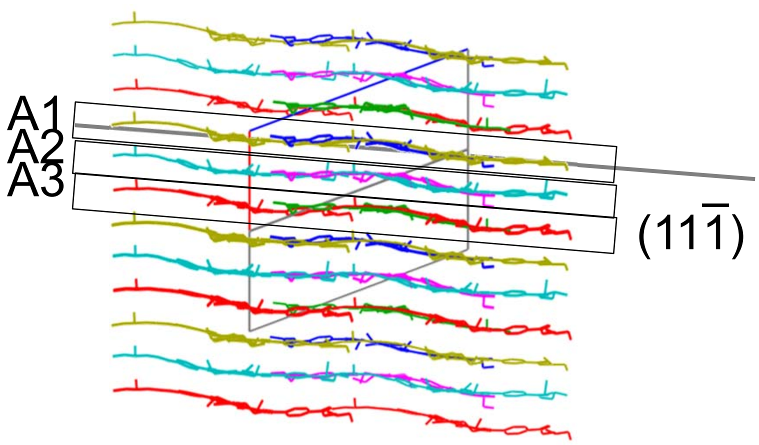
b = 24.9 Å
c = 25.7 Å
α = 90.9°

One of the
tetramers



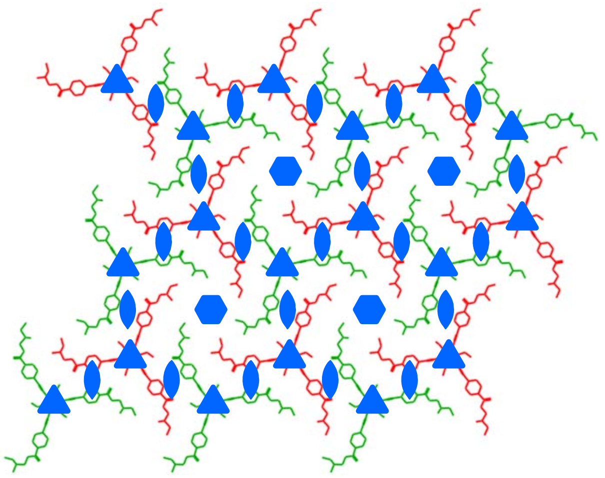
Projection along [1$\bar{1}$0]



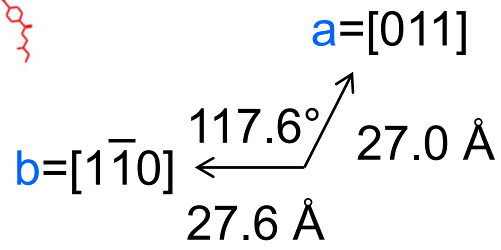


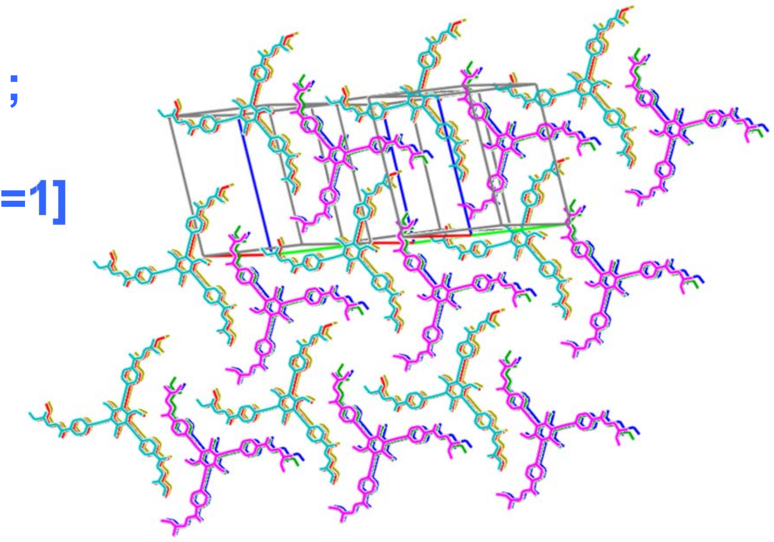
QARNAA
(*P*1, *Z*'=6)

A layer (11$\bar{1}$) (A3) and a superposition of the three layers (11$\bar{1}$) A1, A2 and A3



***p*6 (#73), *z'*=1;**
[almost
***p*6/*m* (#75), *z'*=1]**



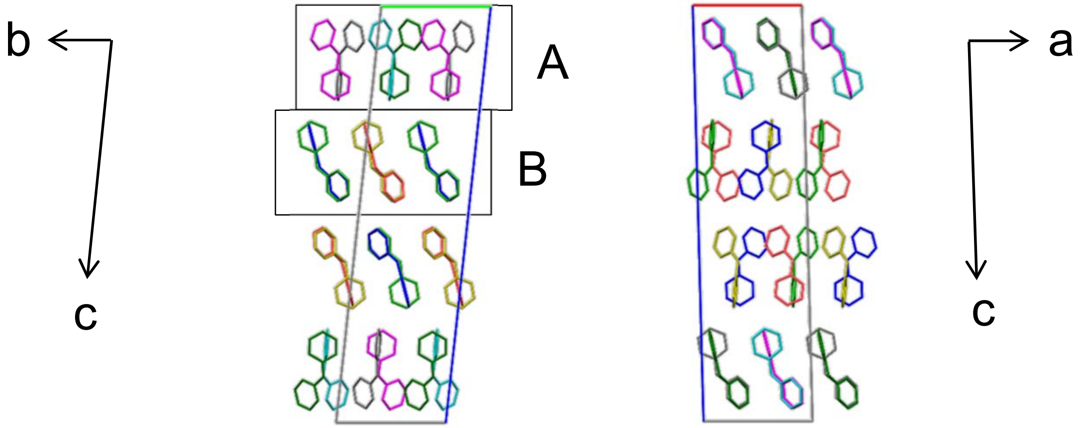


The three layers are related by a pseudotranslation [010]/3

(*p*6 because the three terminal *sec*-Bu groups should make crystal enantiomerically pure, but otherwise the symmetry is almost *p*6/*m*)

Projections along **a** and **b**

QQQBVP02
($P\bar{1}$, Z'=8)

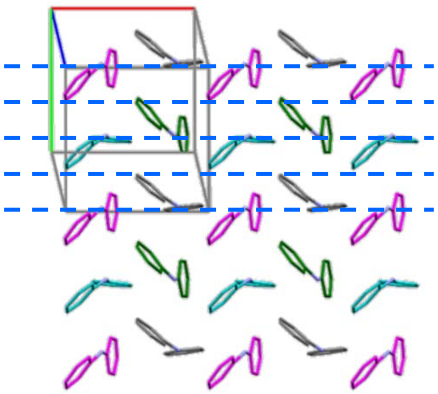


a = 9.85 Å
b = 9.88 Å
α = 89.9°

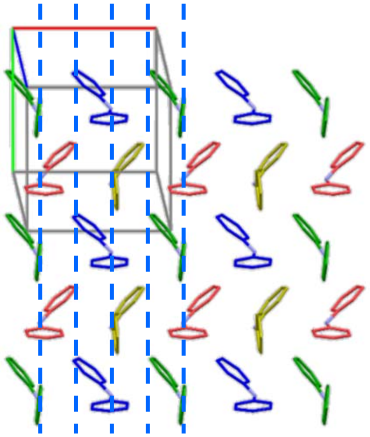
Layers (001) A, B and their superposition after rotation of B

$p1a1$ (#12), z'=1

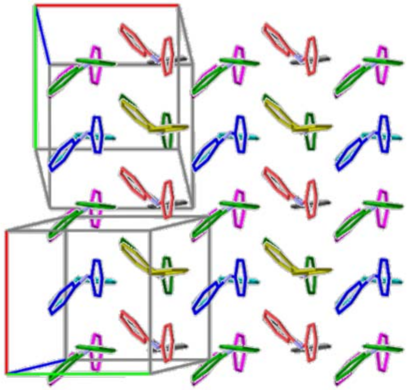
$pb11$ (#12), z'=1



pseudotranslation
b/2



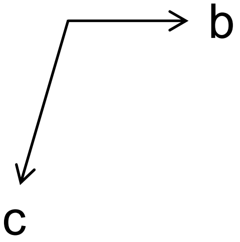
pseudotranslation
a/2

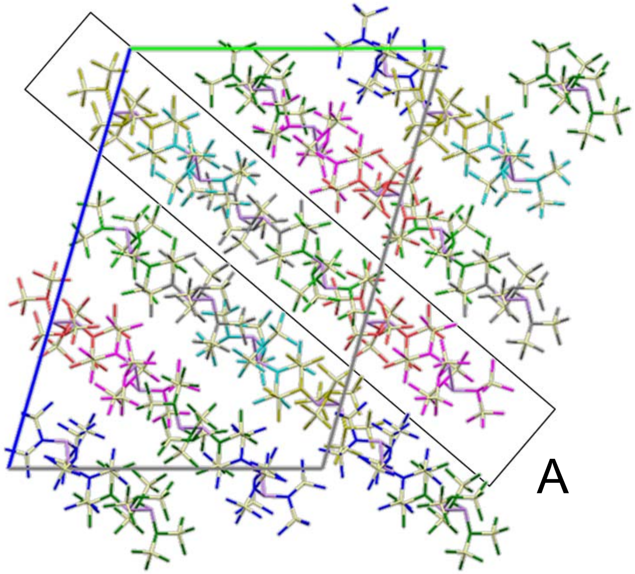


(the two layers are a little different)

Projection along **b**

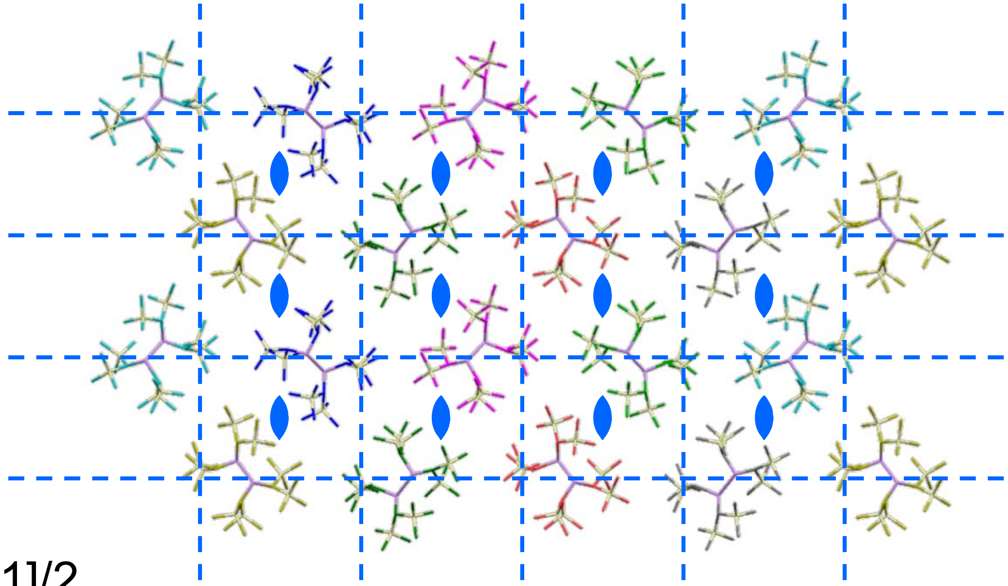
QUQQUO
($P\bar{1}$, Z'=8)



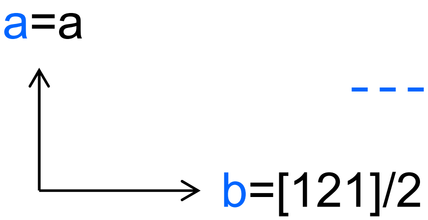


Layer $(0\bar{1}2)$: A

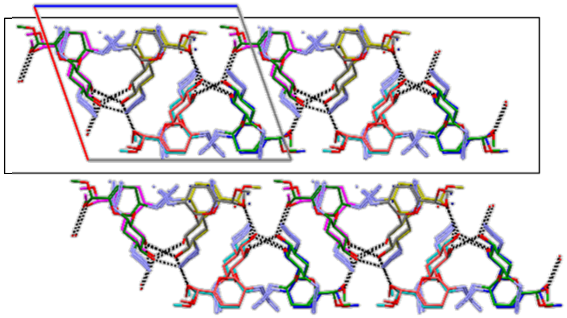
$pba2$ (#44), z'=1



pseudo translation [121]/2

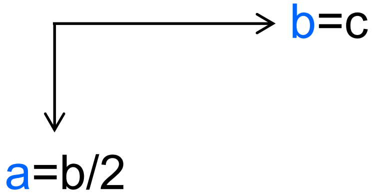


Projection along **b**

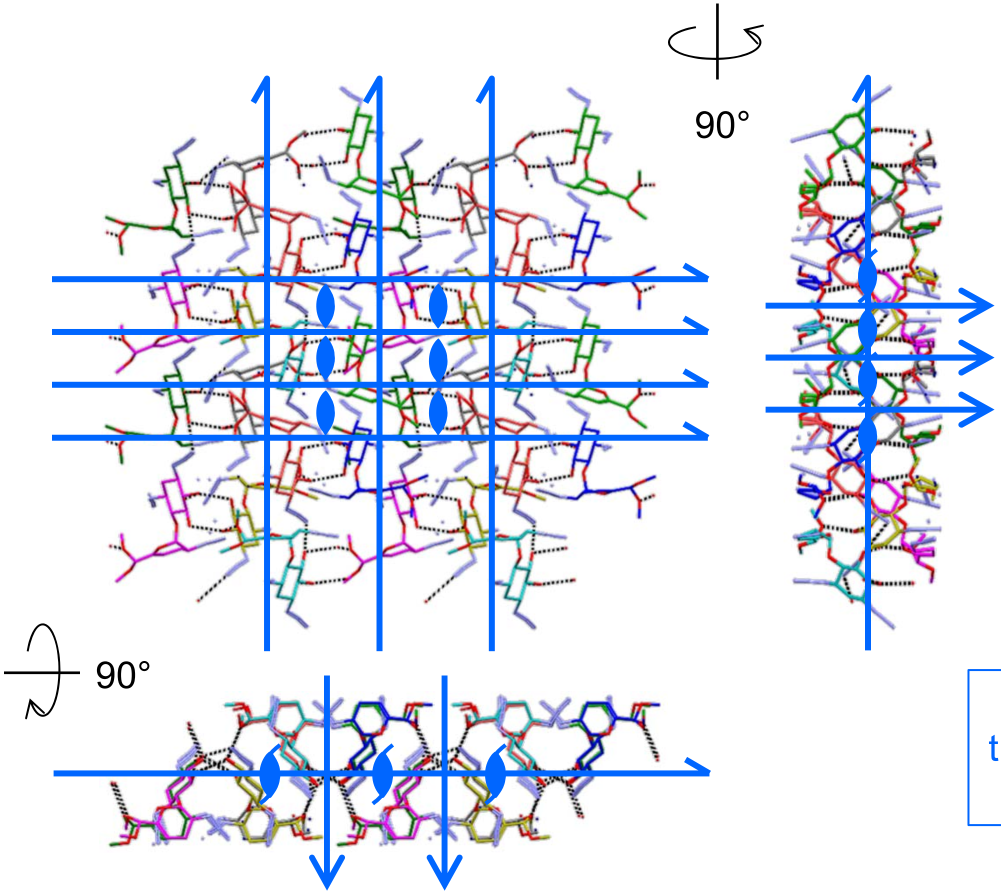


RAKBUC
($P1$, Z'=8)

Layer (001)



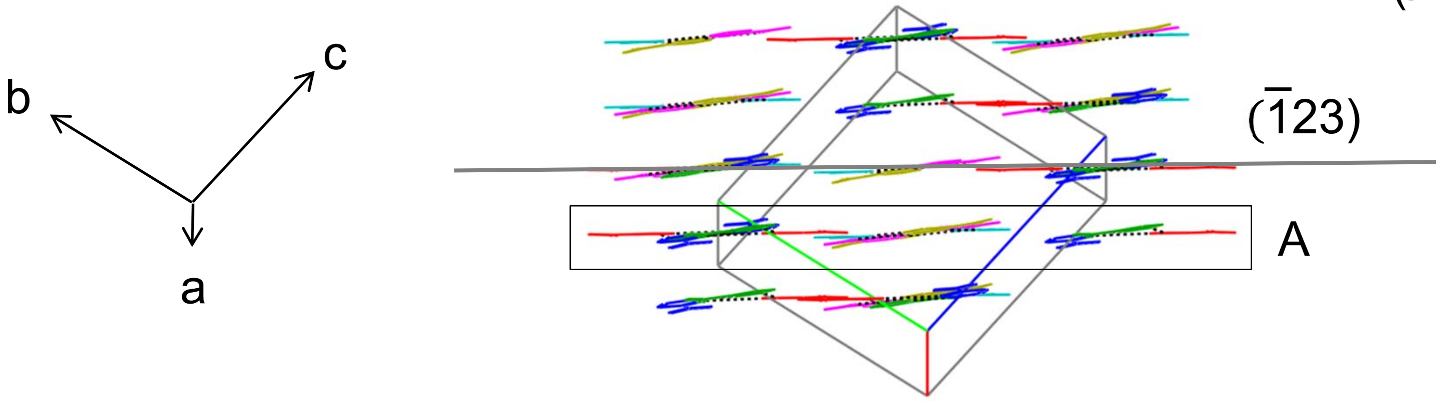
$p2_12_12$ (#21),
z'=1



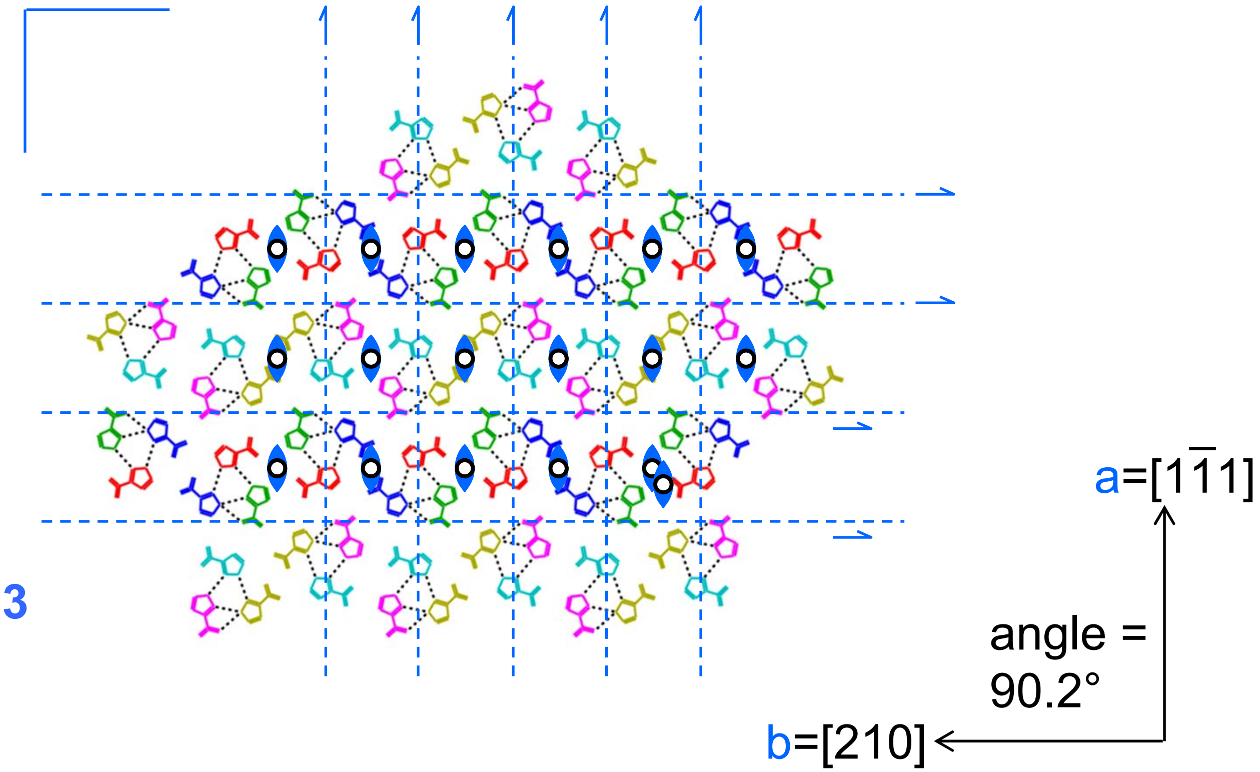
pseudo translation **a**/2

Projection along $(\bar{1}23)$ and [511]

RIKNOO
($P\bar{1}$, Z'=6)



Layer $(\bar{1}23)$

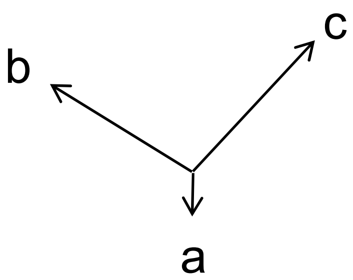


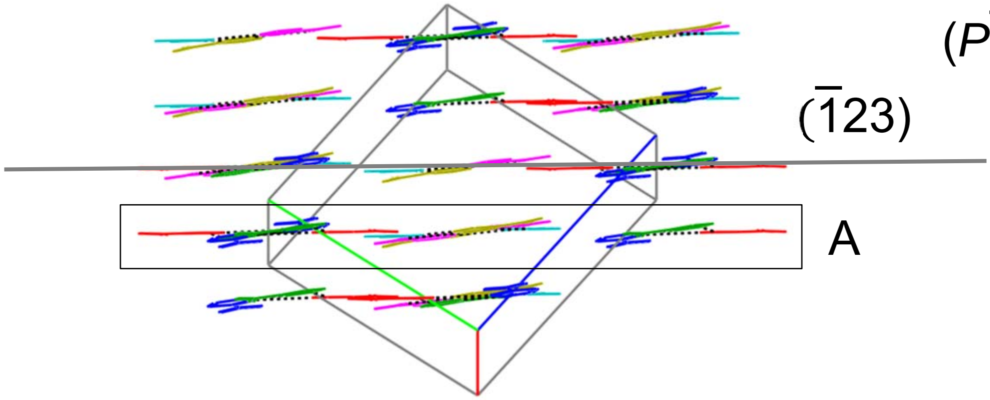
***pbam* (#44), *z'*=3**
($\bar{1}$ s exact)

(see also next page)

Projection along $(\bar{1}23)$ and [511]

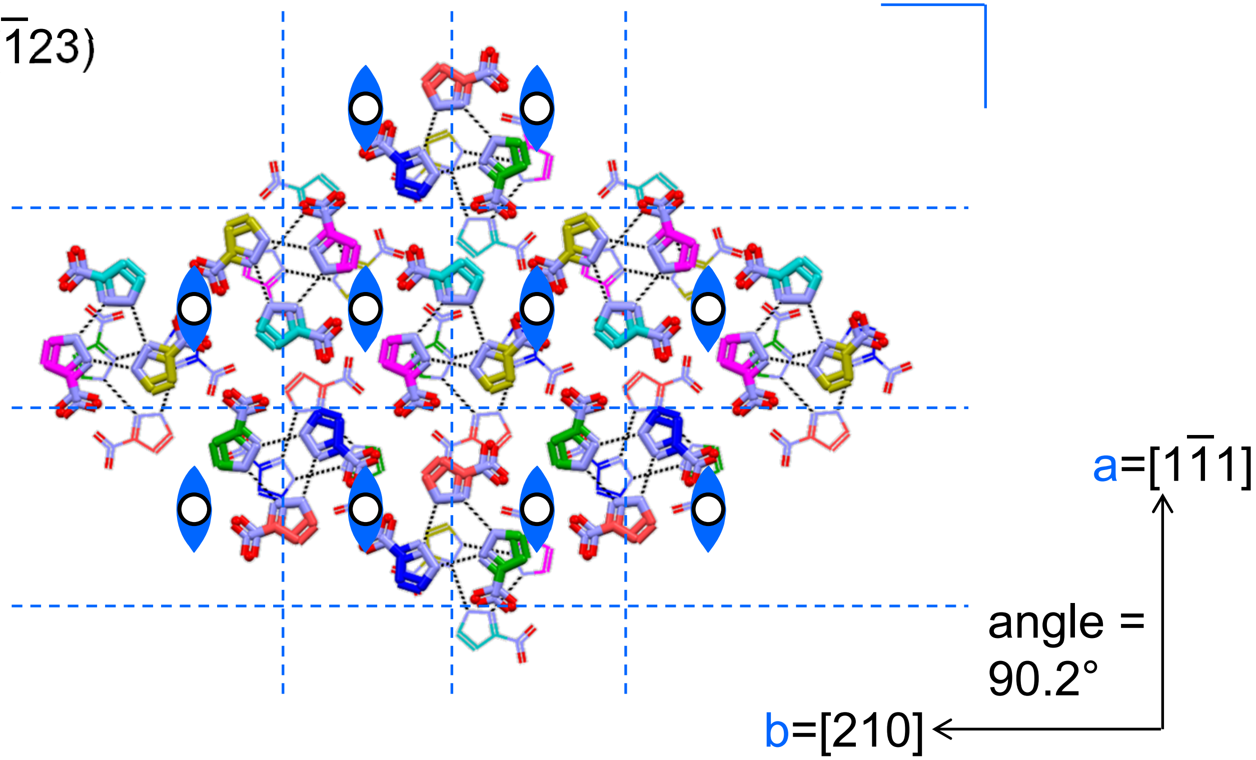
RIKNOO
con't
($P\bar{1}$, Z'=6)





Two adjacent layers $(\bar{1}23)$

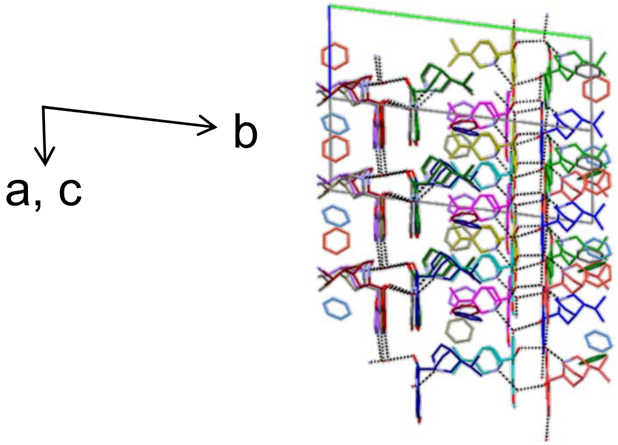
***pbam* (#44), *z'*=3**
($\bar{\mathbf{1}}$ s exact)

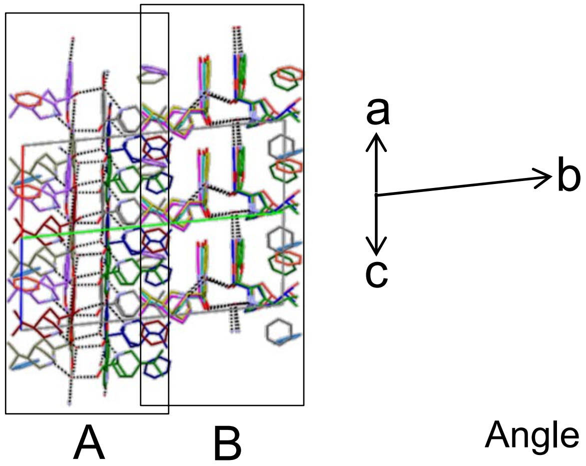


Adjacent layers are related by inversion centers that are not aligned with the approximate glides

Projections along $[10\bar{1}]$ and [101}

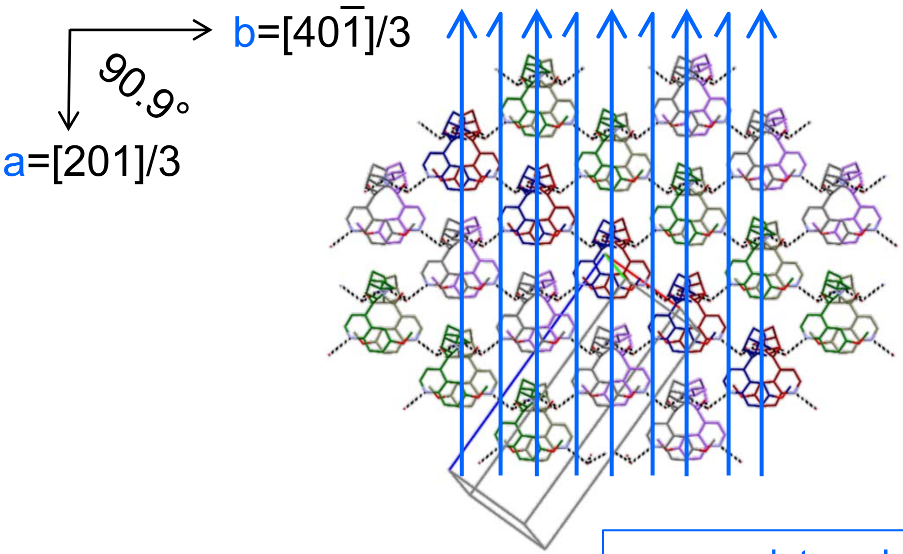
RUKTOI
($P1$, Z'=12)

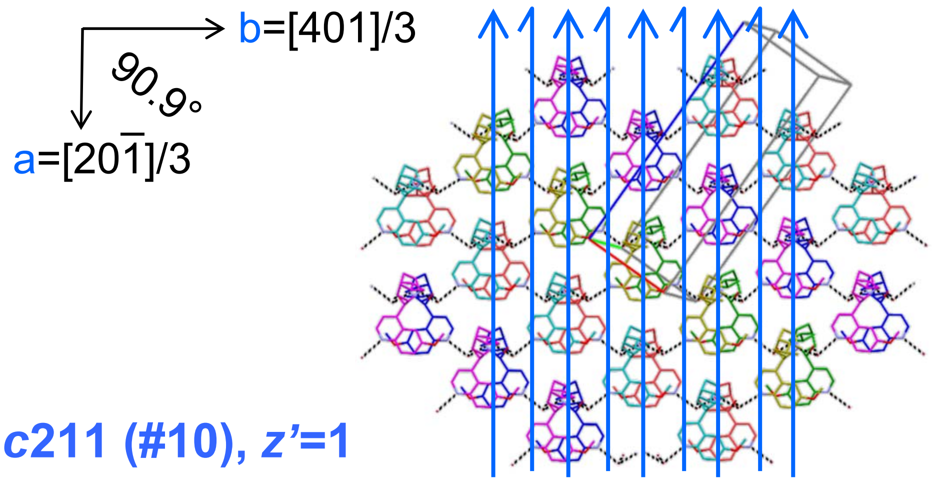




Layers (010) A, B

Angle between [201]
and {$20\bar{1}$] is 69.6°





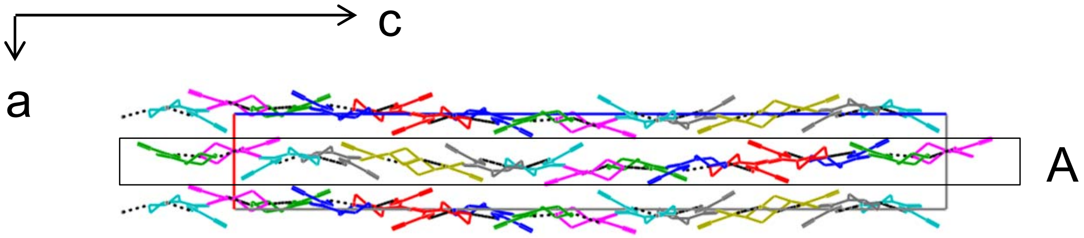
***c*211 (#10), *z'*=1**

pseudotranslations
$[10\bar{1}]/3$, $[201]/3$ & $[40\bar{1}]/3$

pseudotranslations
$[101]/3$, $[20\bar{1}]/3$ & $[401]/3$

Projection along **b**

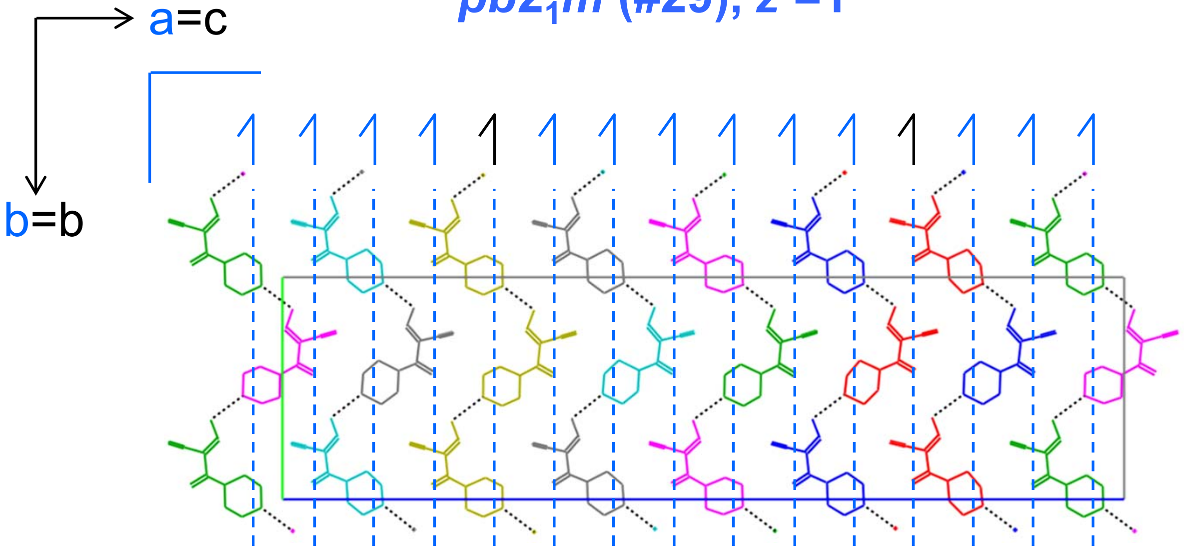
SABPOB
($P2_12_12_1$, Z'=7)



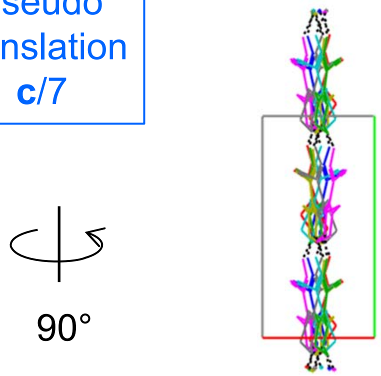
Layer (100)

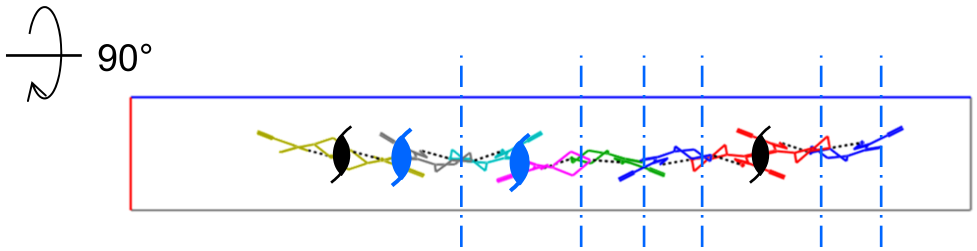
***pb*2$_1$*m* (#29), *z*'=1**

[layer group would be *pb*2$_1$*a* (#33), *z*'=1 if *Z'* were even and the 2$_1$, glide alternation were perfect]



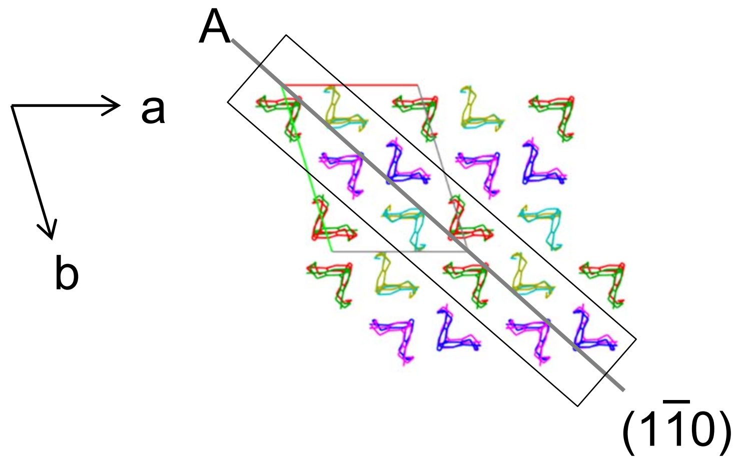
pseudo translation **c**/7



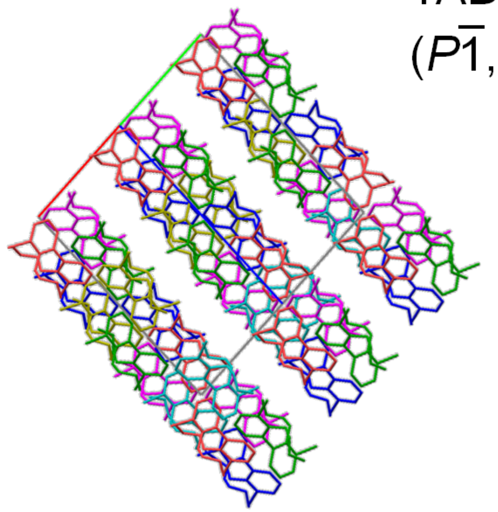


the lower drawing shows how the approximate 2_1 axes and *b* glides alternate in the non-planar layer

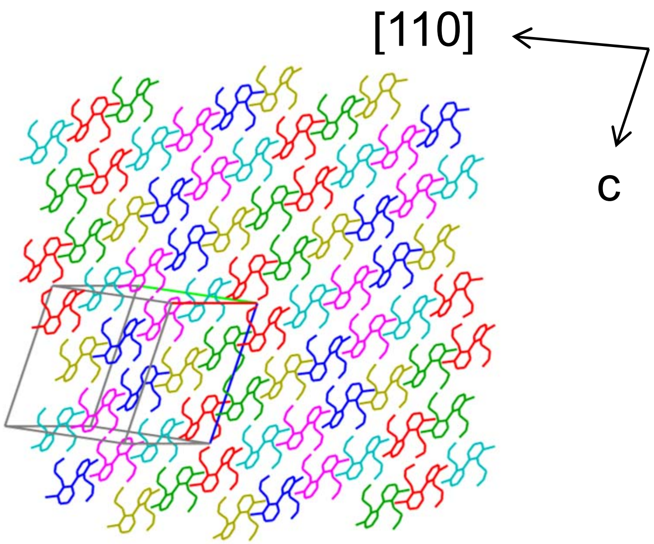
Projections along **c** and along [110]



TADWIH
($P\bar{1}$, Z'=6)

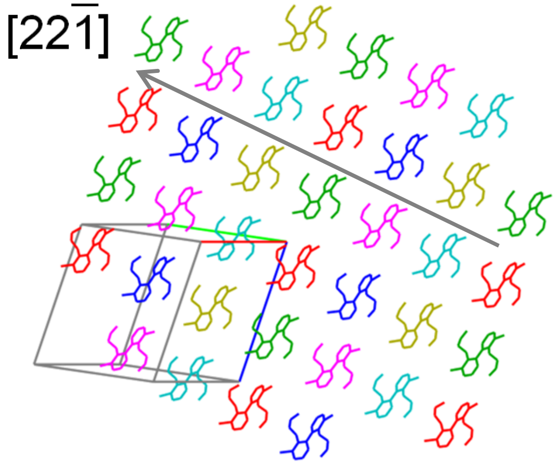


Bilayer ($1\bar{1}0$) and one half of the bilayer



***p*112/*a* (#7)**

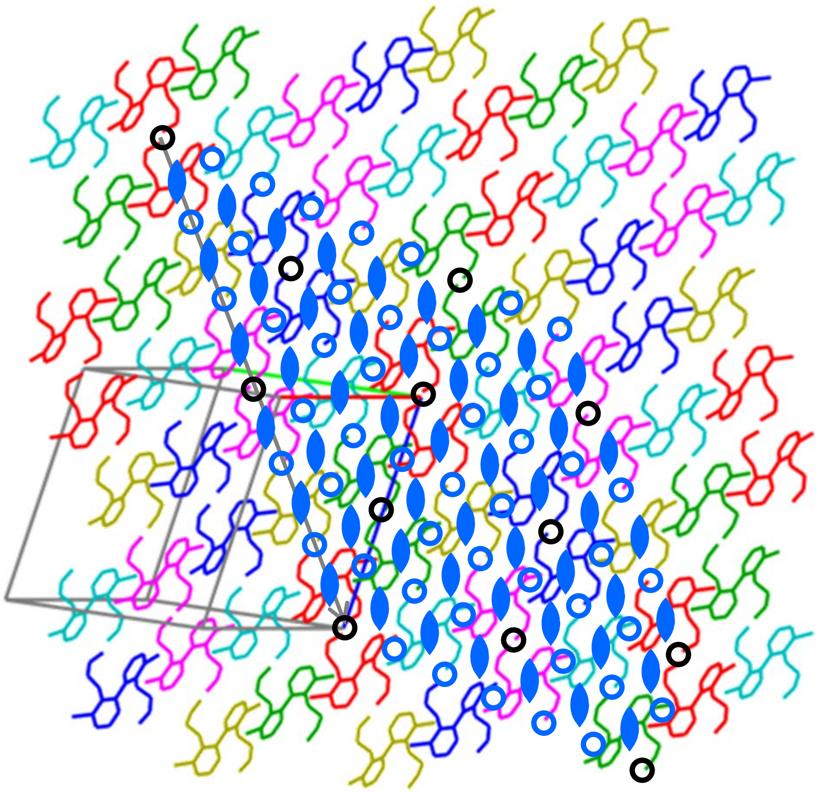
pseudo
translation
[$22\bar{1}$]/6



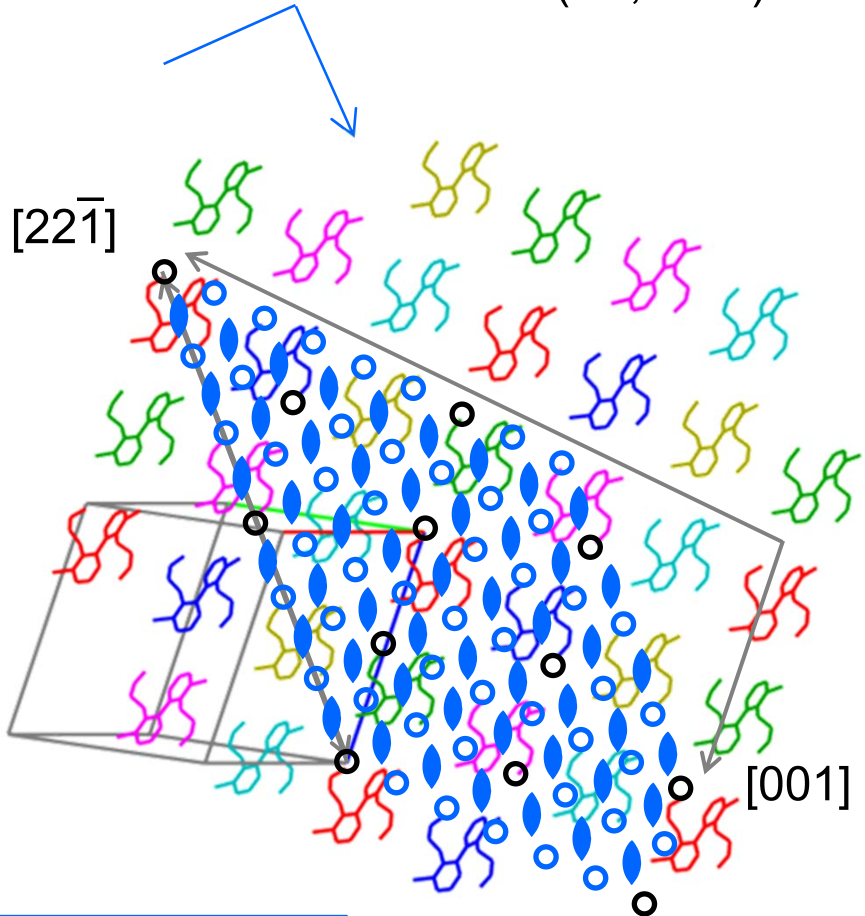
(see next page)

Bilayer $(1\bar{1}0)$ A and one half of the bilayer

TADWIH,
con't
($P\bar{1}$, Z'=6)



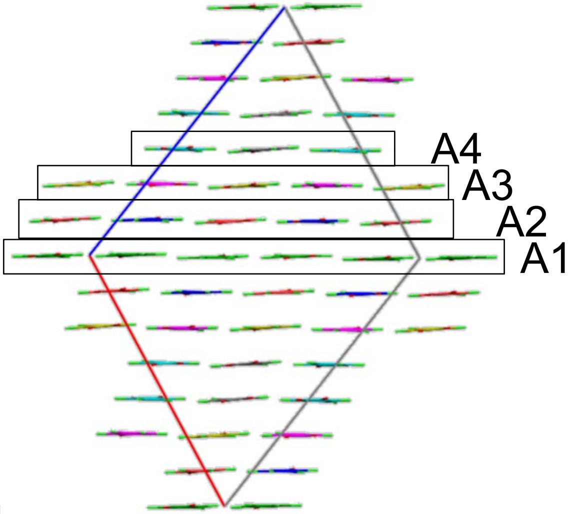
***p112/n* (#7, standard setting *p112/a*), *z'*=½; axes $[22\bar{1}]$/6 and [001]/2**



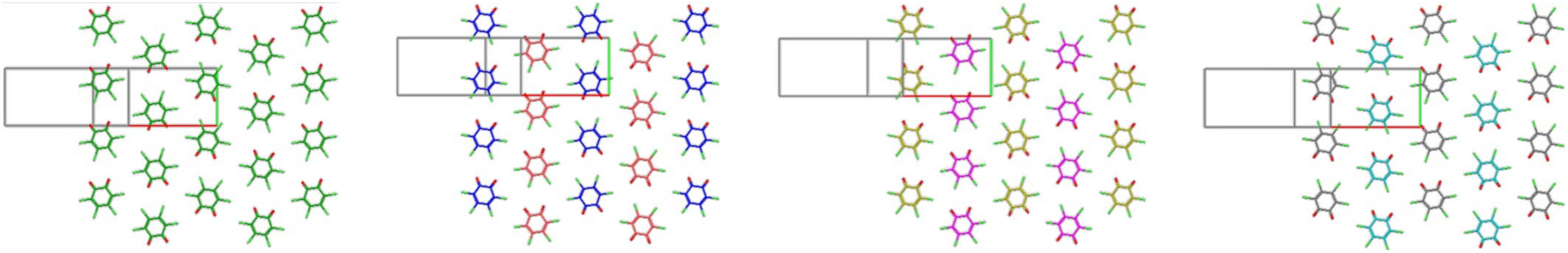
pseudotranslation
$[22\bar{1}]$/6
(and [111]/3, [001]/2)

Projection along **b**

TCLOBQ01
($P2_1/n$, Z'=7)

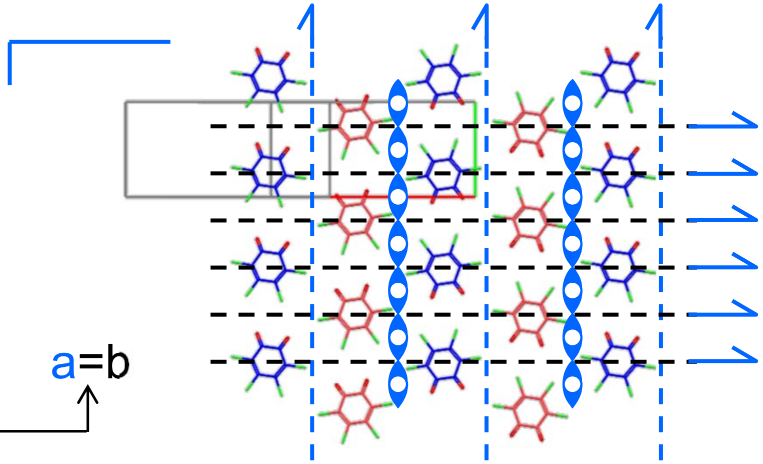


Layers (10$\bar{1}$) A1, A2, A3, A4



***pbam* (#44), *z'*=1**

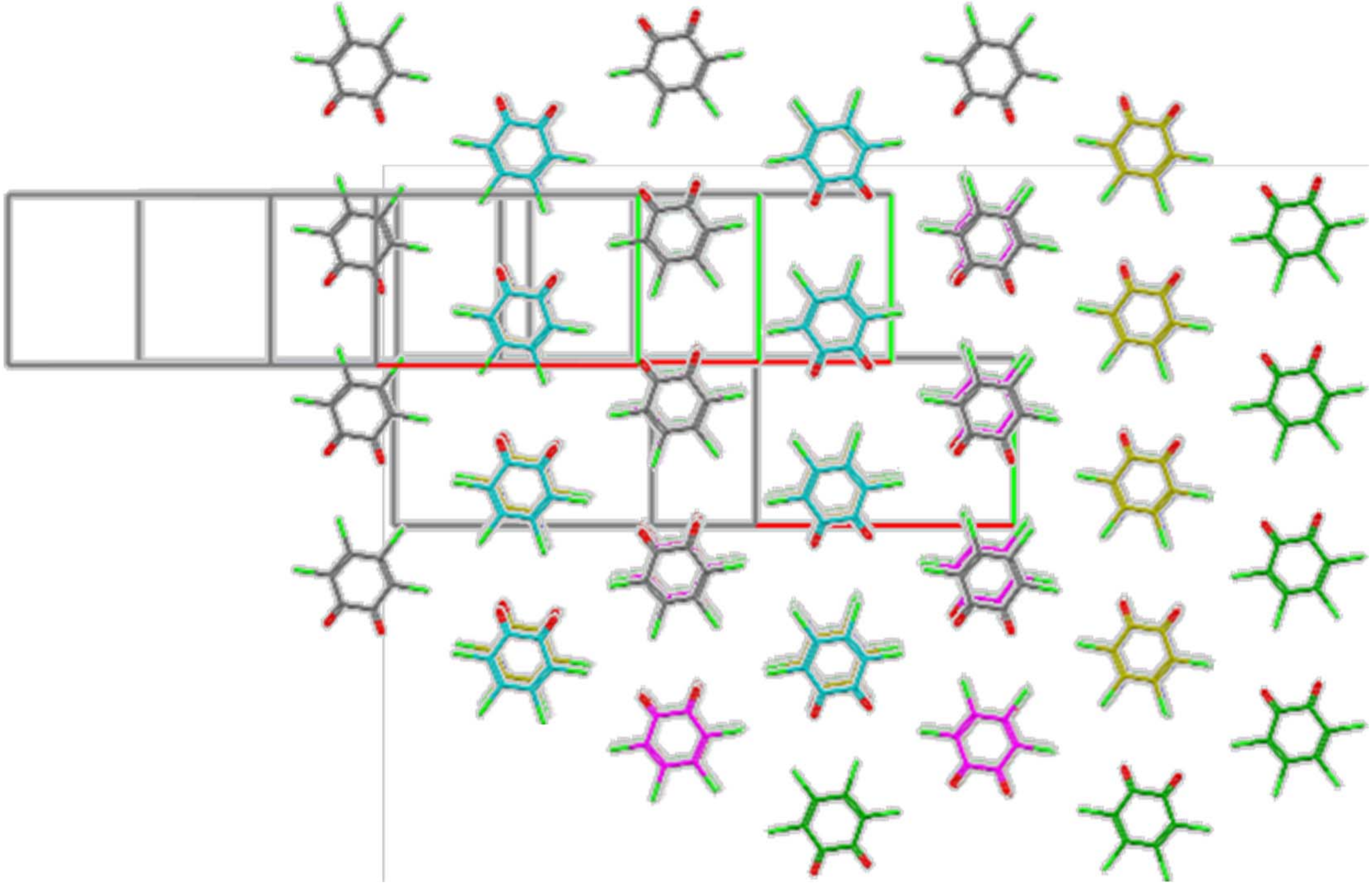
(glides along b=[101] are exact in all layers; inversion centers and 2_1 axes along a=**b** are exact in layer A1)



(superposition by translation of the four layers is shown on the next page)

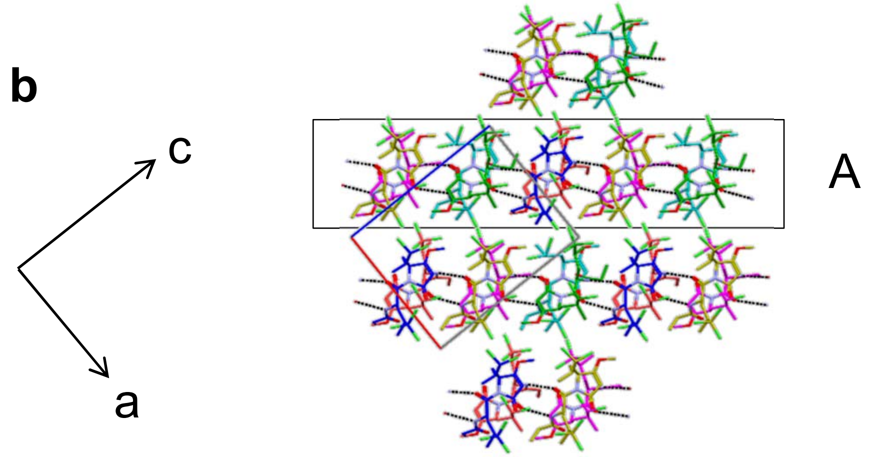
Superposition by translation of the four layers ($10\bar{1}$)

TCLOBQ01,
con’t
($P2_1/n$, Z'=7)

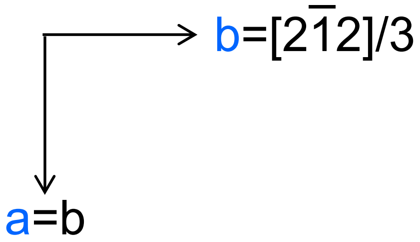


TORHAK
(*P*1, *Z'*=6)

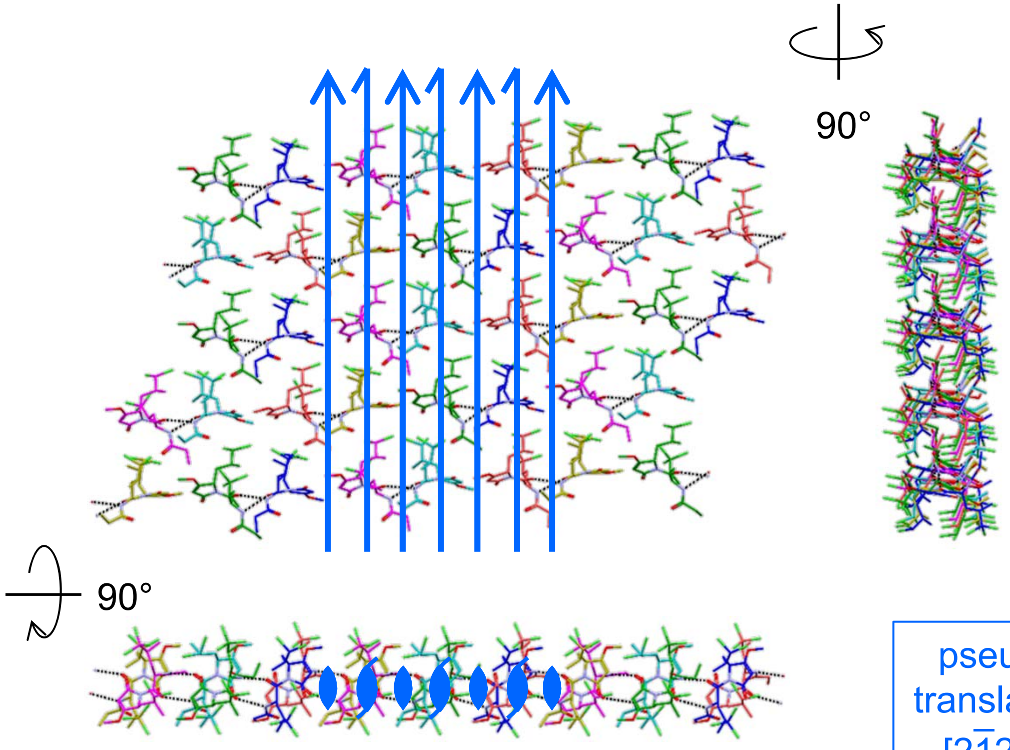
Projection along **b**



Layer (10$\bar{1}$)

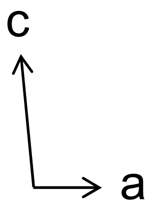


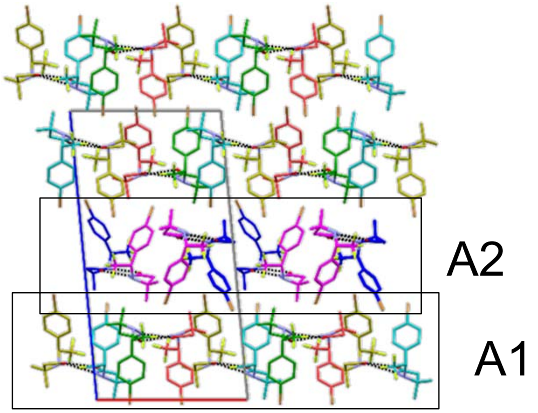
***c*211 (#9),**
***z'*=1**



pseudo
translation
[2$\bar{1}$2]/3

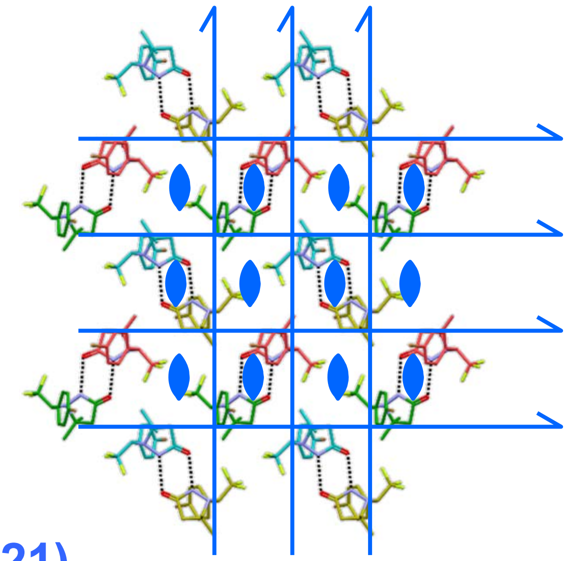
Projection along **b**





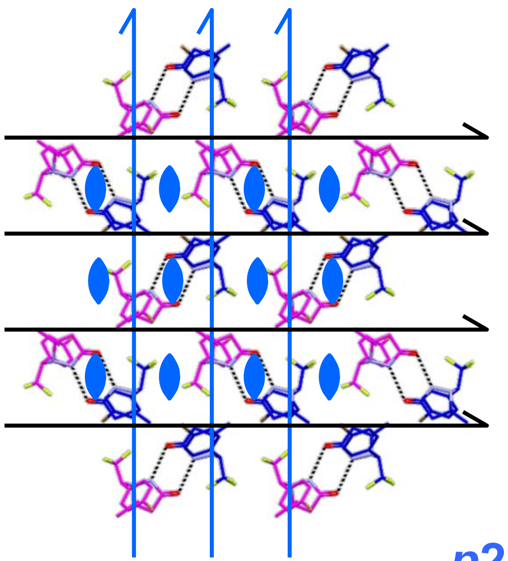
UHIPAD
($P2_1$, Z'=6)

Layers (001): A1 at z = 1/4 and A2 at z = 1/2



$p2_12_12$ (#21),
z'=1

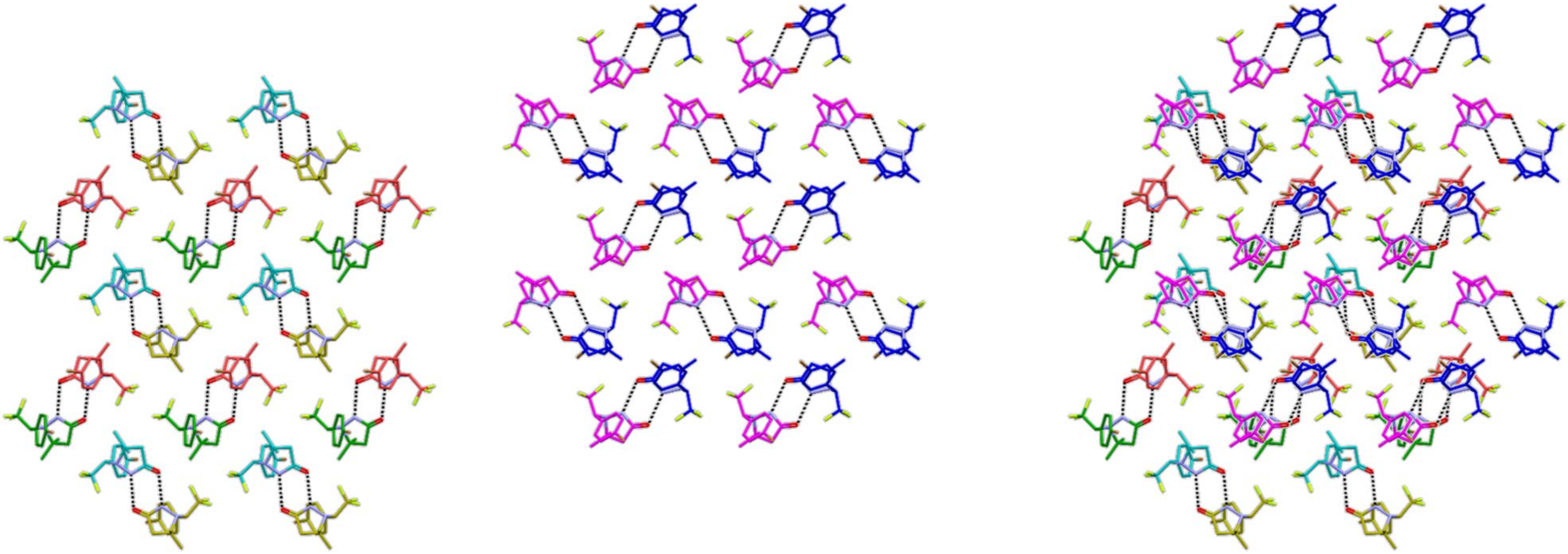
(see next page)



$p2_12_12$ (#21),
z'=1

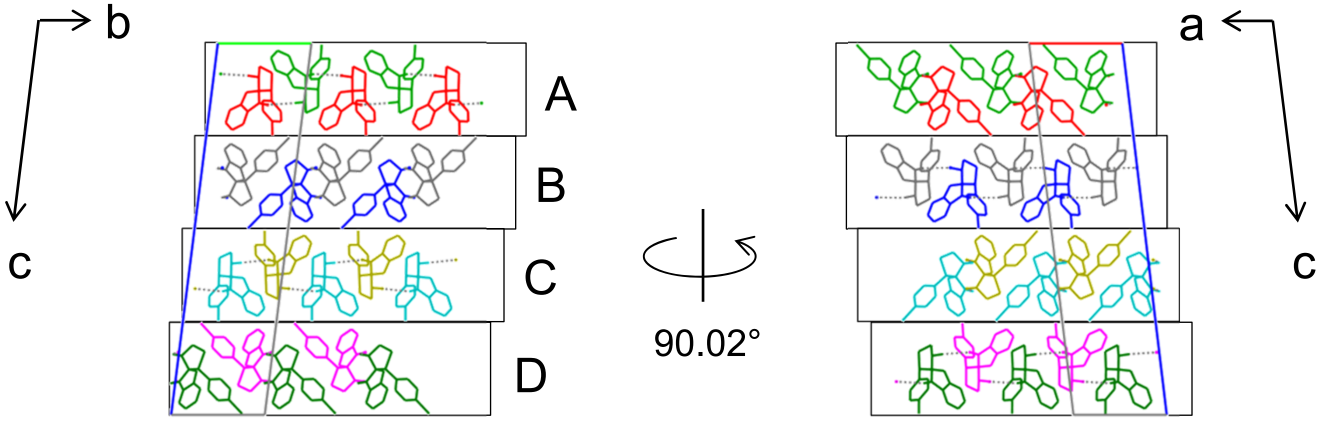
Layers (001): A1 at $z = 1/4$ and A2 at $z = \frac{1}{2}$ and their superposition by translation

UHIPAD,
con't
($P2_1$, Z'=6)



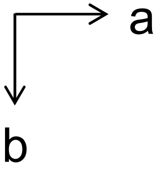
Projections along **a** and **b**

UMAHAT
($P1$, Z'=8)



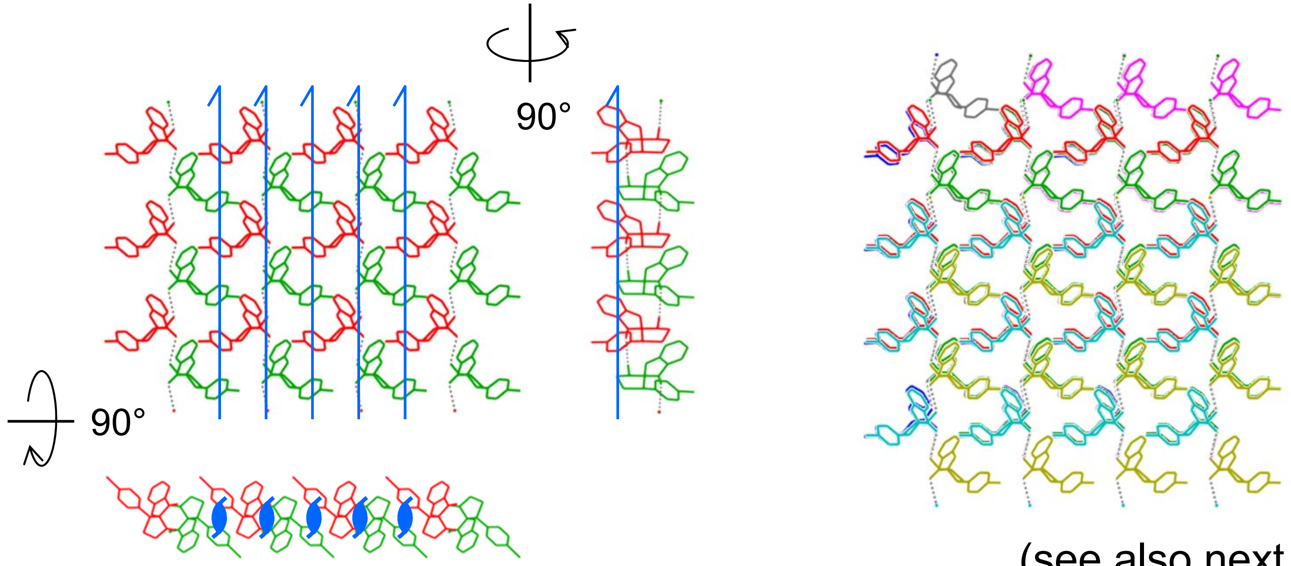
α =97.1°
β =96.8°

Layers (001): A and a superposition (with translations) of all four layers after rotations of 0° (A), 90° (B), 180° (C), and 270° (D) around c*



A,C/ $p12_11$
B,D/ $p2_111$
all (#9), z'=1

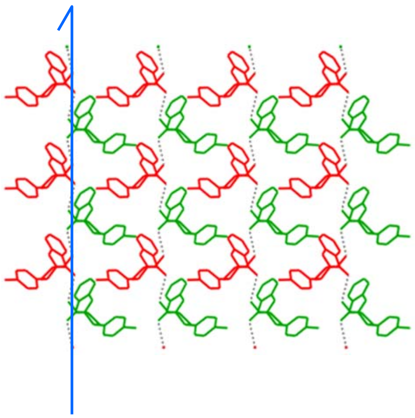
a = 9.18 Å
b = 9.22 Å
γ = 90.0°



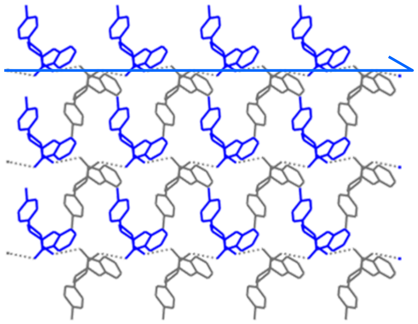
(see also next two pages)

Projections along **a** and **b** of layers (0 0 1): A, B, C and D

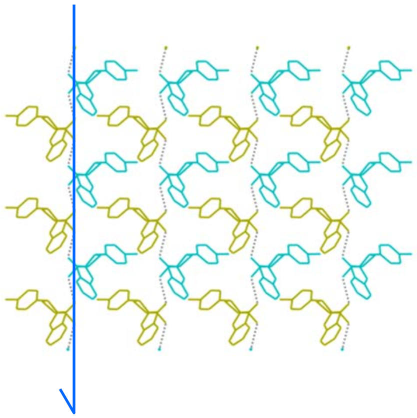
UMAHAT,
con't
(*P*1, *Z*'=8)



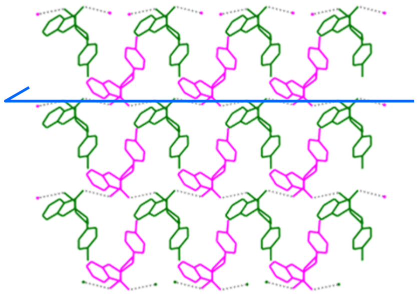
$p12_11$ (#9), z'=1



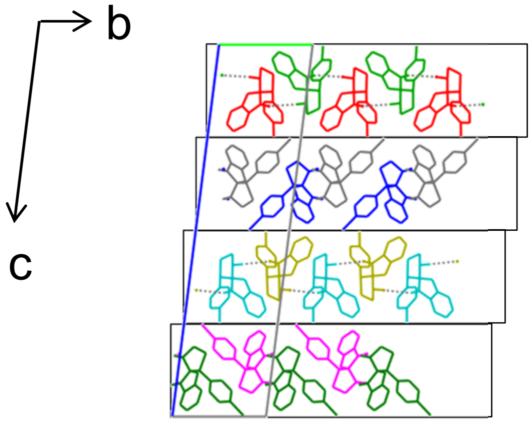
$p2_111$ (#9), z'=1



$p12_11$ (#9), z'=1



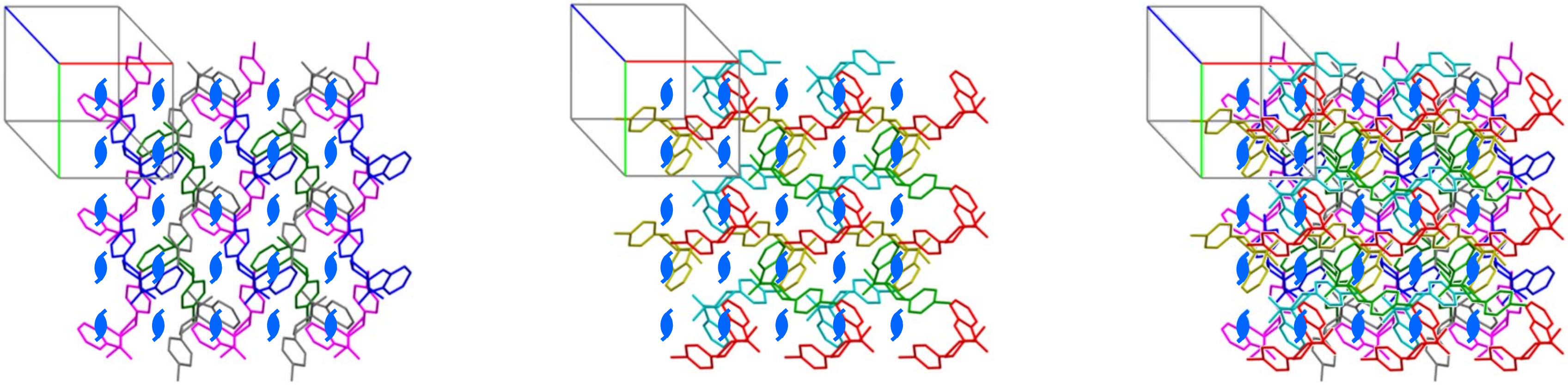
$p2_111$ (#9), z'=1



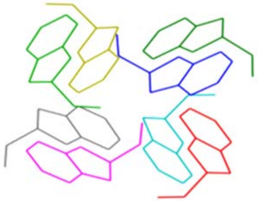
(see also next page)

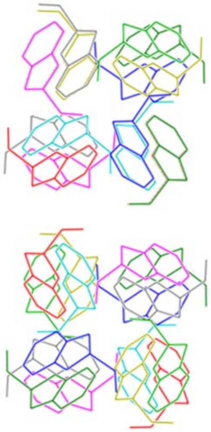
UMAHAT, yet again ($P1$, $Z'=8$)

Projections along **c*** to show that layers separated by $\Delta z \cong \frac{1}{2}$ are related by approximate 2_1 axes and that the two sets of screw axes are superimposable [overall approximate space group $P2_1$ (#4)]

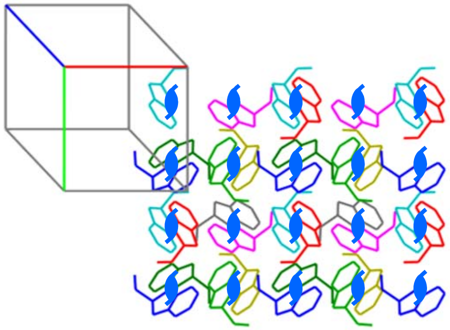


Projections along **c*** with part of the molecule deleted to show that there is no fourfold axis and that **c*** is close to [1 1 2], along which the structure is periodic



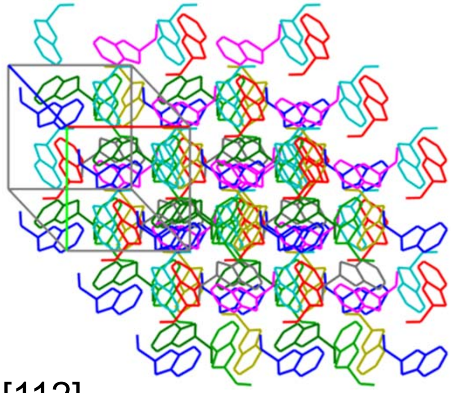


A group of 8 molecules and superpositions of two sets after rotations by 90° and 180°



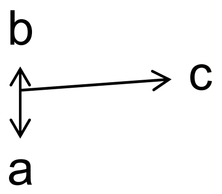
$0 \le z \le 1$

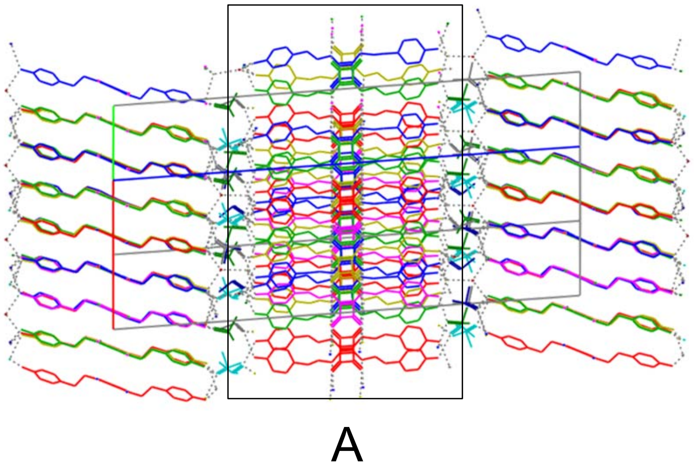
Angle of [112] with **c*** is 0.34°



$0 \le z \le \mathbf{3}$

Projection along [120]

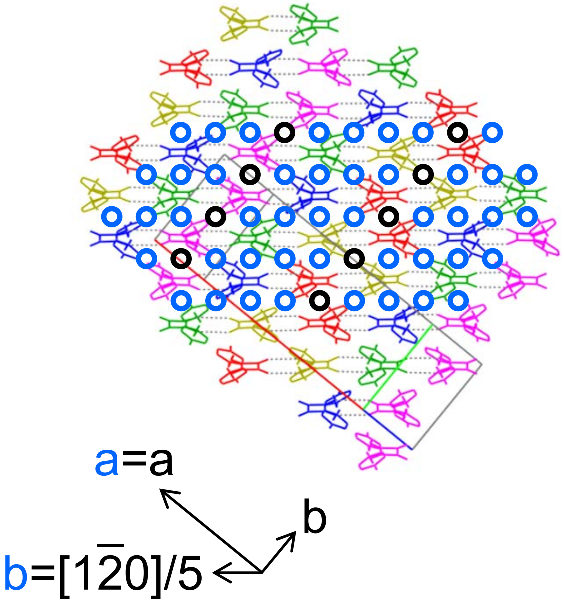


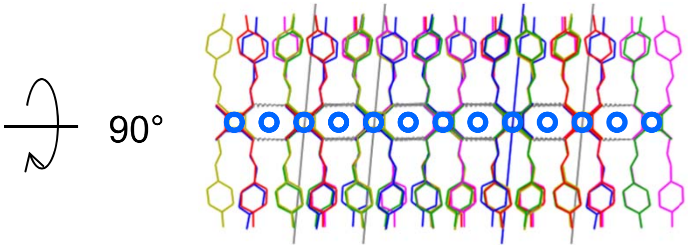


WOPVOO
($P2_1/c$, $Z'=5$)

Angle [120], [$1\bar{2}0$] is 78.7°;
angle [120], (010) is 50.6°.

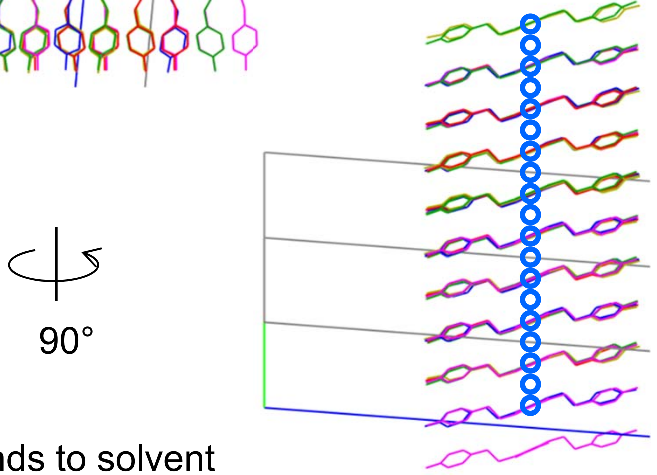
Layer (001) at $z=½$ (solvent molecules not shown)





$p\bar{1}$ (#2),
$z'=5$

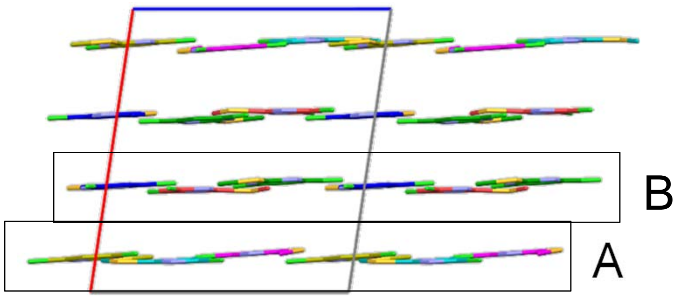
pseudo
translation
[$1\bar{2}0$]/5

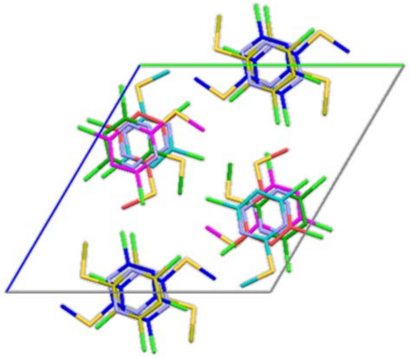


(H-bonds to solvent
molecules not shown)

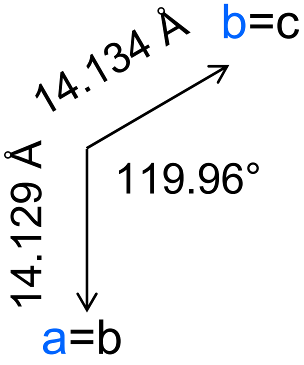
Projections along **b** and **a**

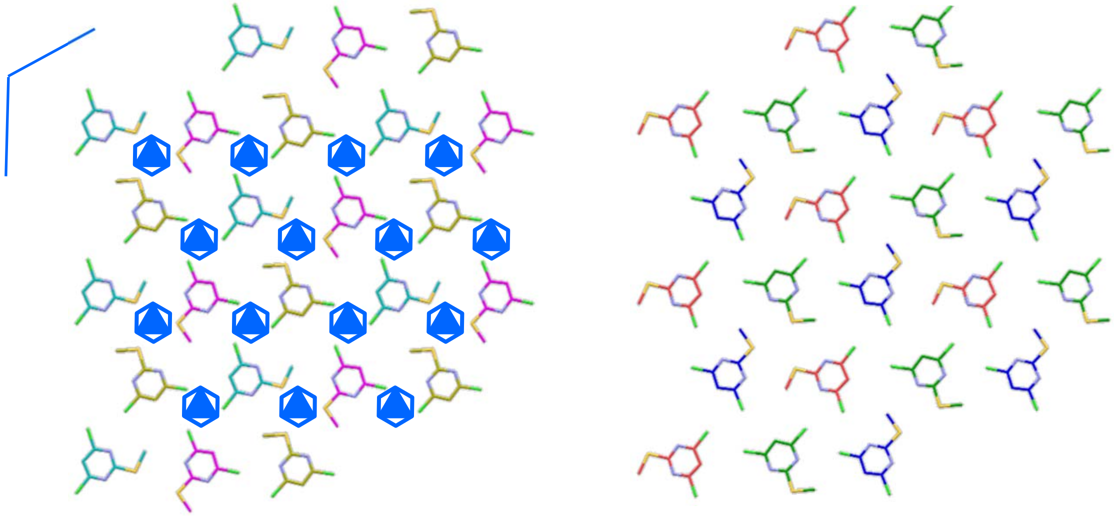
XAXTUL
($P\bar{1}$, Z'=6)





Layers (100) A and B





***$p\bar{6}$* (#74), *z'*=1**

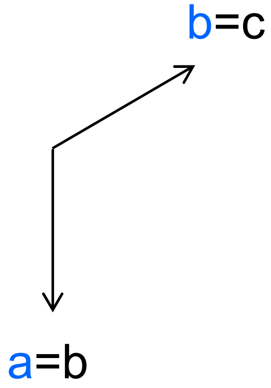
(see next page)

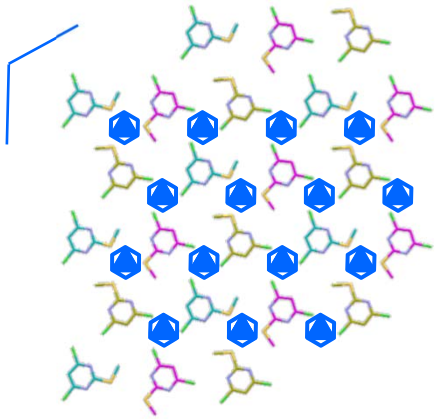
Layers (100) A and B
and their superposition without and with rotation of B

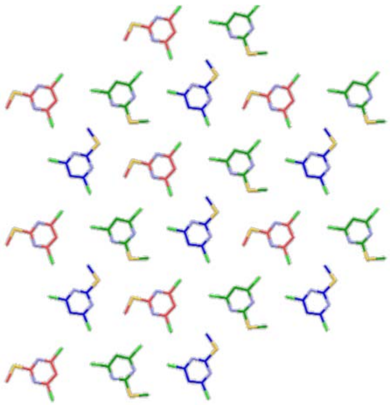
XAXTUL,
con't
($P\bar{1}$, Z'=6)

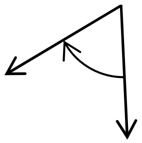
A

B



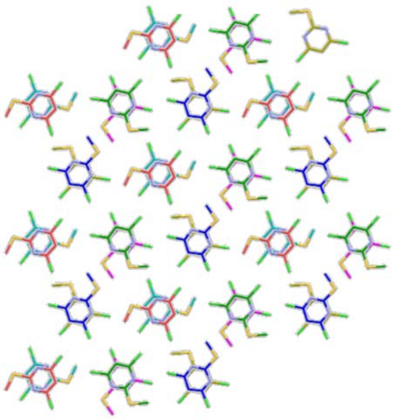


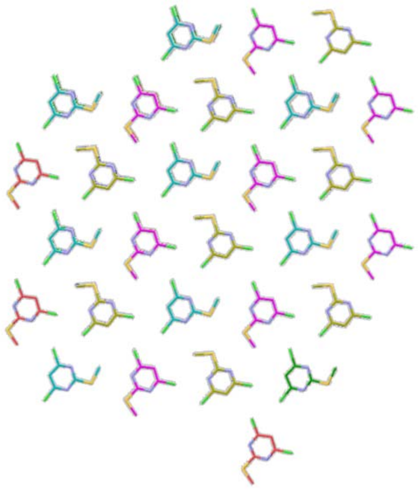




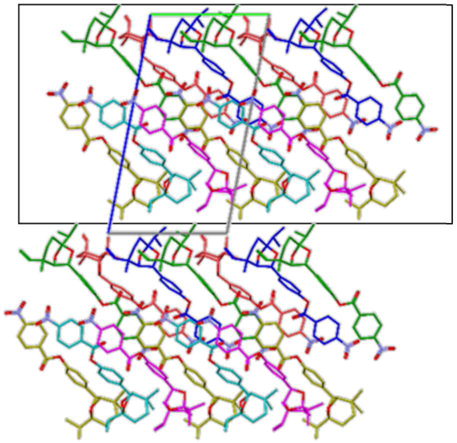
A, B
superposition
without rotation

A, B superposition with
rotation of B by the angle
shown



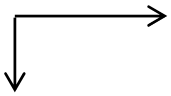


Projection along **a**



XODGAA
($P1$, Z'=6)

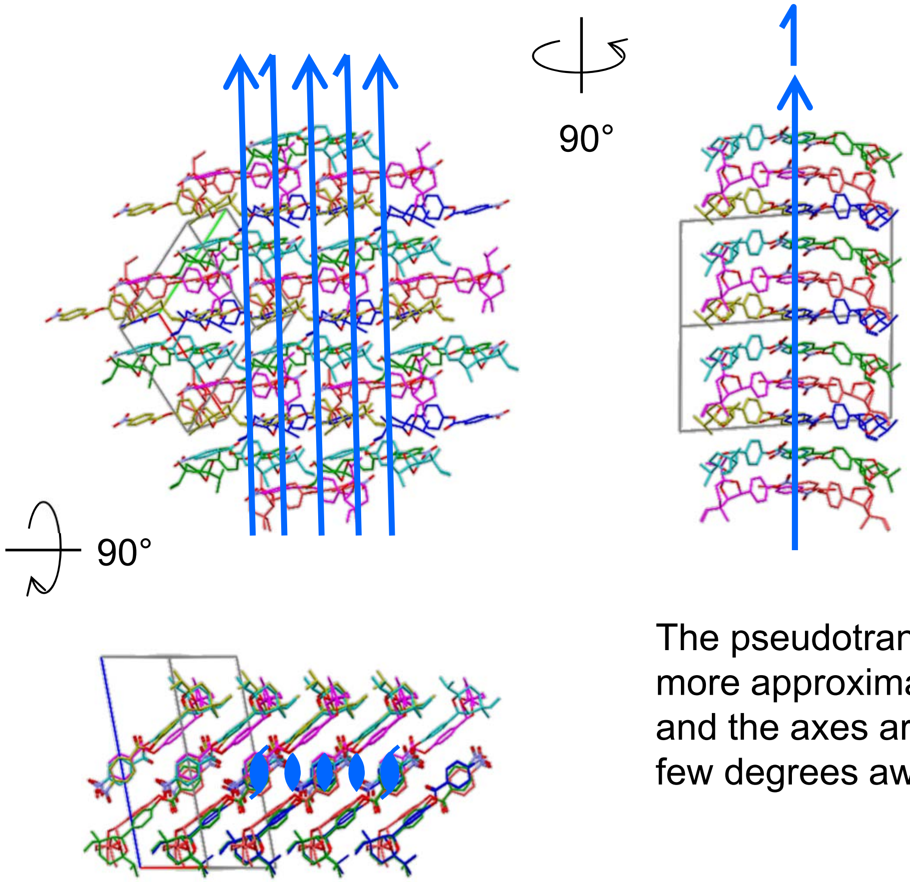
Layer (001)



b=[110]

a=$[1\bar{1}0]/3$

$c2_1$ (#9),
z'=1

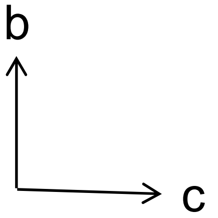


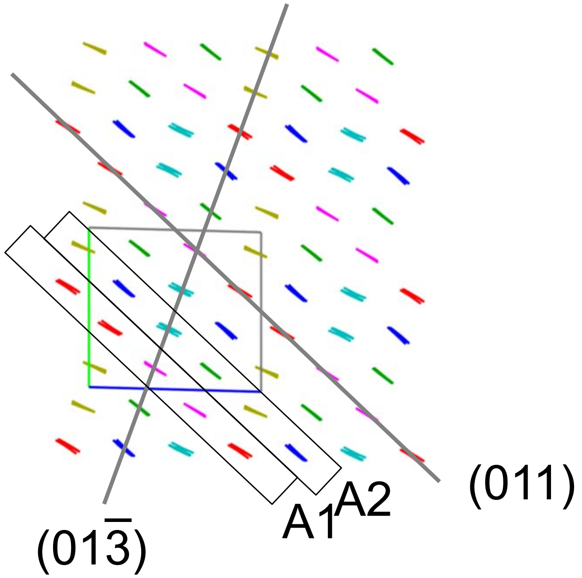
pseudo
translation
$[1\bar{1}0]/3$

The pseudotranslation is more approximate than many and the axes are rotated a few degrees away from a.

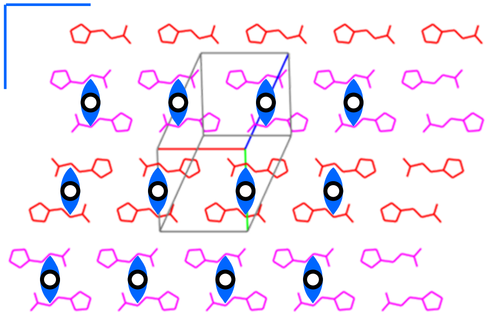
Projection along **a**

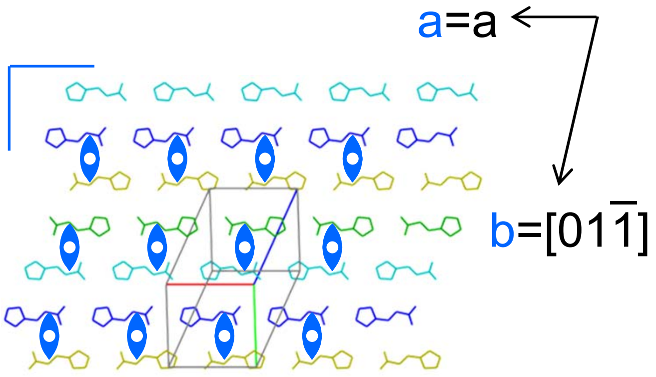
XOZBUK01
($P\bar{1}$, Z'=6)

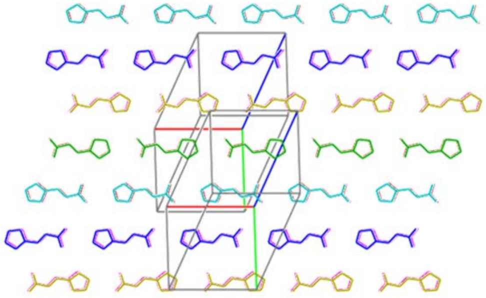




Layers (011): A1, A2 and their superposition by translation





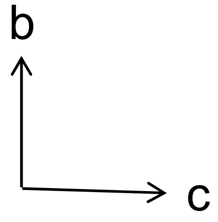


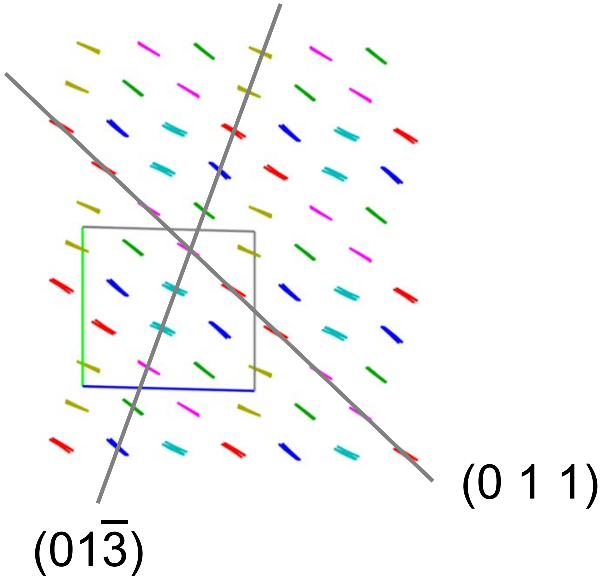
$p112/m$ (#6), z'=2
(1-bars exact)

$p112/m$ (#6), z'=2

(see also next page)

Projection along **a**

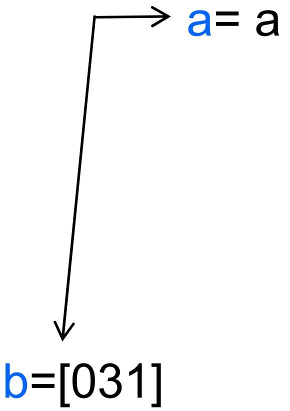


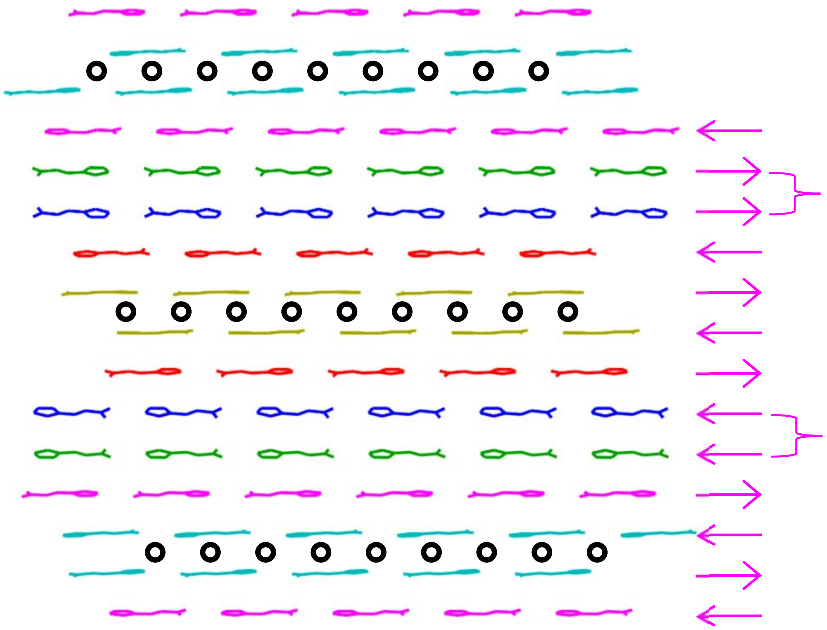


XOZBUK01, con’t ($P\bar{1}$, Z'=6)

(011) Is a better choice than $(01\bar{3})$ because (011) has higher approx.-imate symmetry

Layer $(01\bar{3})$

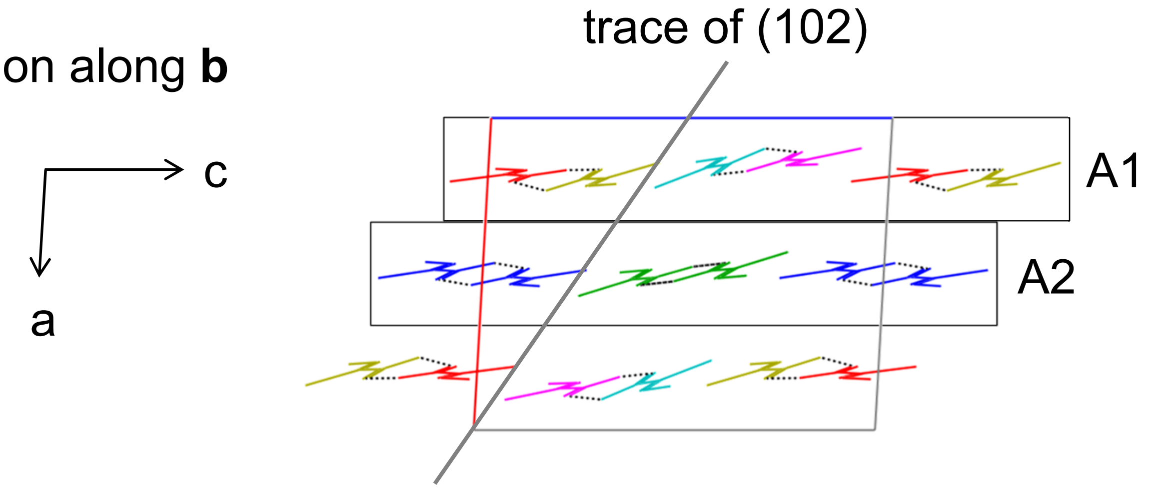




Alternation fault affecting the directions of the long molecular axes

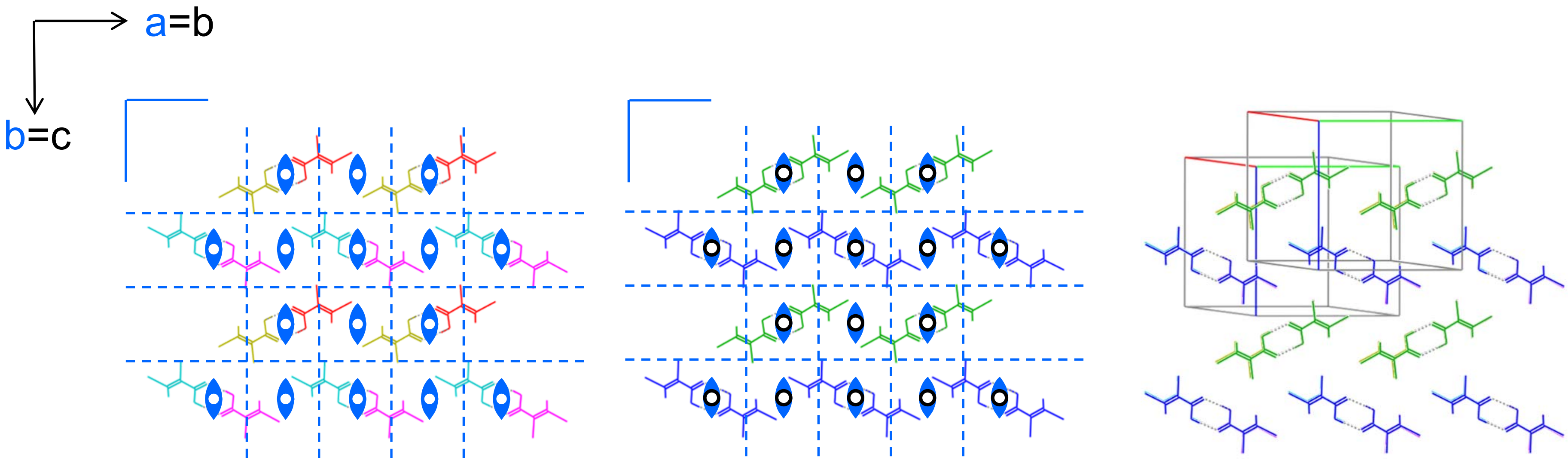
$p\bar{1}$ (#2), z'=6

Projection along **b**



YEZDEN
($P\bar{1}$, Z'=6)

Layers (100) A1 and A2, and their superposition by translation

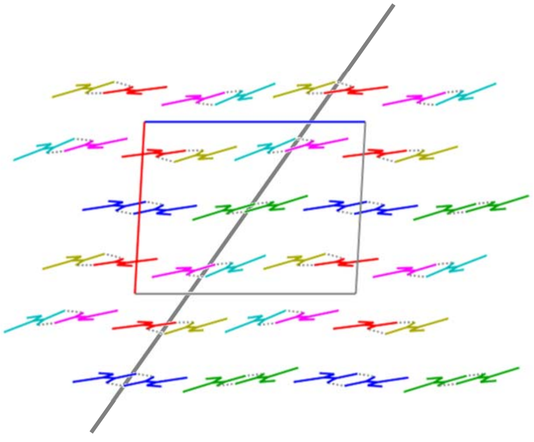


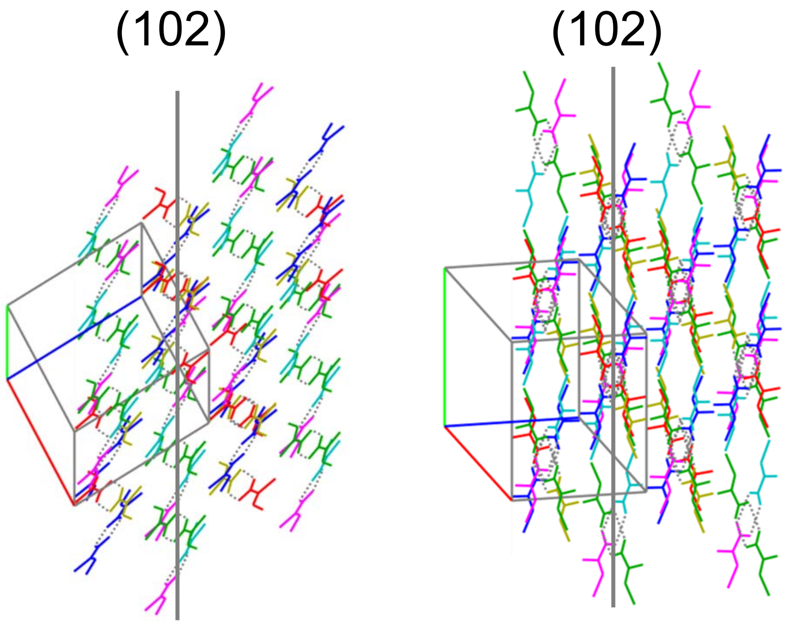
***pbam* (#44), *z'*=1** (1-bars exact in A2)

(see also next page)

Is a (102) layer important?
(Probably not)

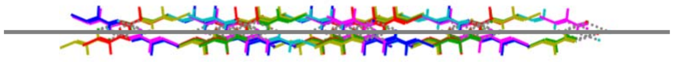
YEZDEN,
con't
($P\bar{1}$, Z'=6)

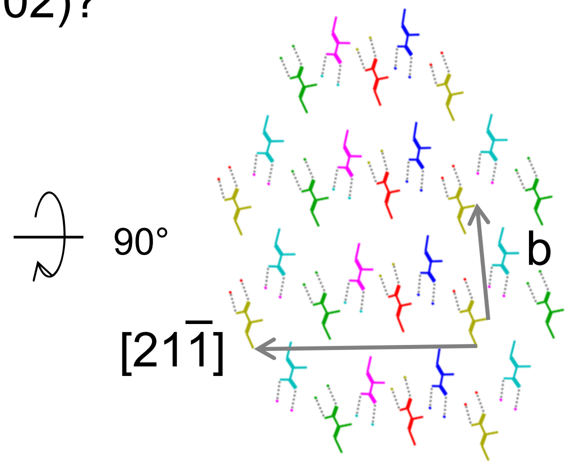




two views related by a *ca* 50° rotation around the horizontal

A pseudotranslation in a layer (102)?

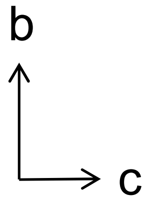


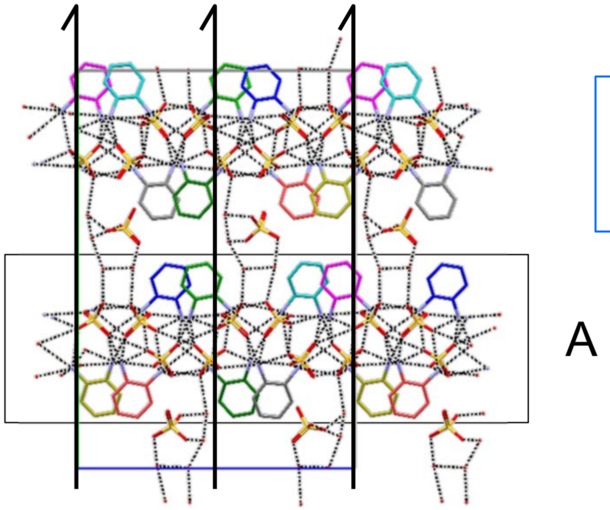


$p\bar{1}$ (#2), z'=2, c'=[21$\bar{1}$]/3
1/3rd of 1-bars exact

[only the bottom half of the slice (102) is shown so that the pseudo-translation is easier to see]

Projection along **a**

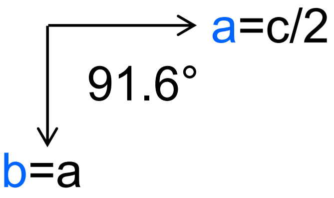


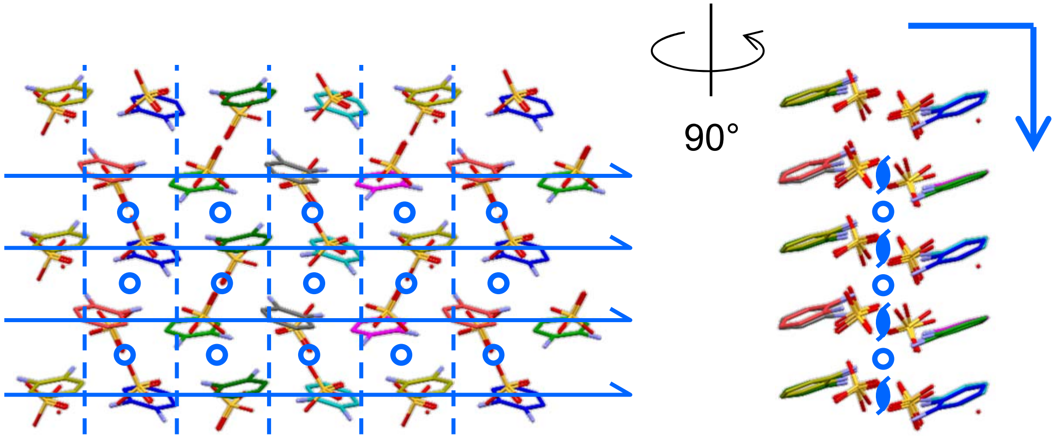


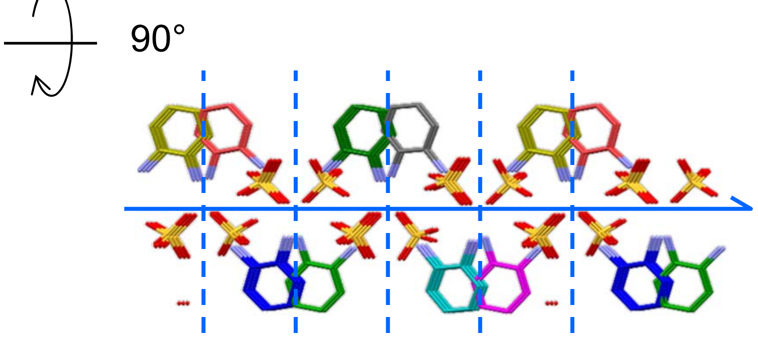
pseudo translation **c**/2

ZATLAJ03 ($P2_1$, Z'=8)

Layer (0 1 0): A



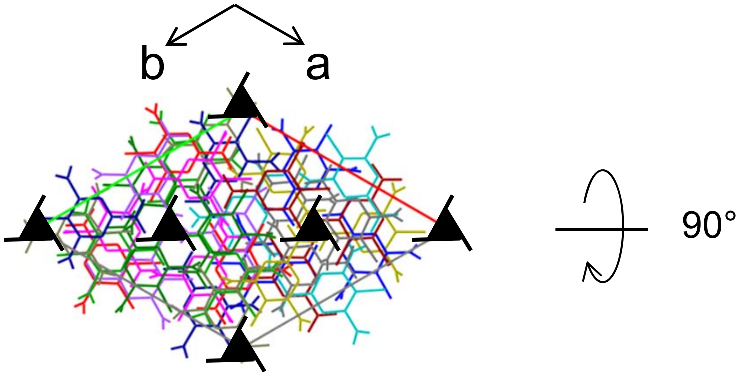




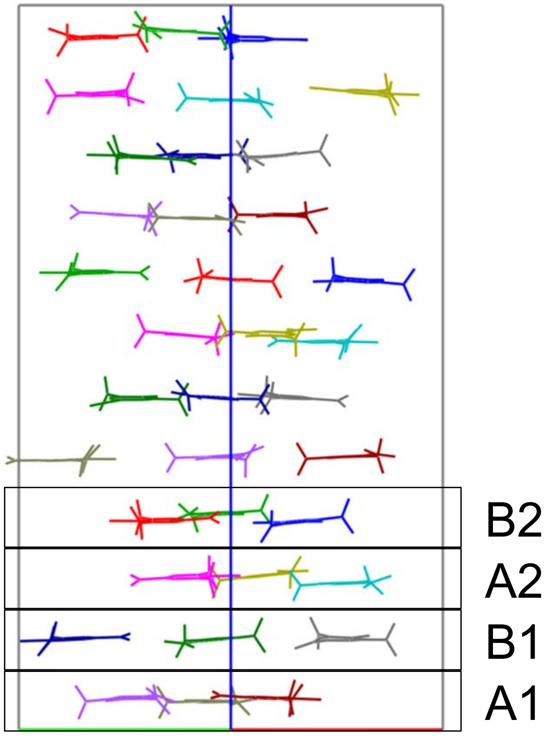
$p2_1/b11$ (#17), z'=1

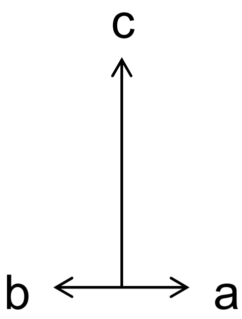
ZATLAJ03 was determined at 120 K. At 130 K (ZATLAJ01) the space group is also $P2_1$ but **c** is half as long and Z'=4. The approximate layer symmetry is the same and the approximate inversion centers are offset in the same way from the screw axes of $P2_1$.

Projection along **c**

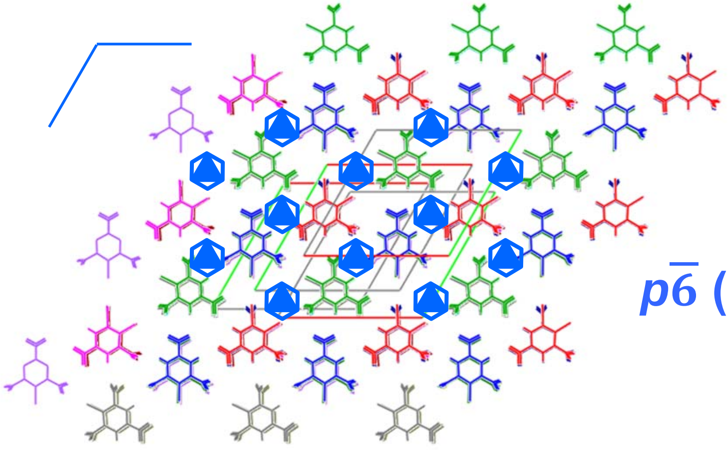


ZZZVXQ02
($P3_1$, $Z'=12$)





Overlay by translation of the four independent layers (001) after rotation of layers B1 and B2 by 180° around the layer normal

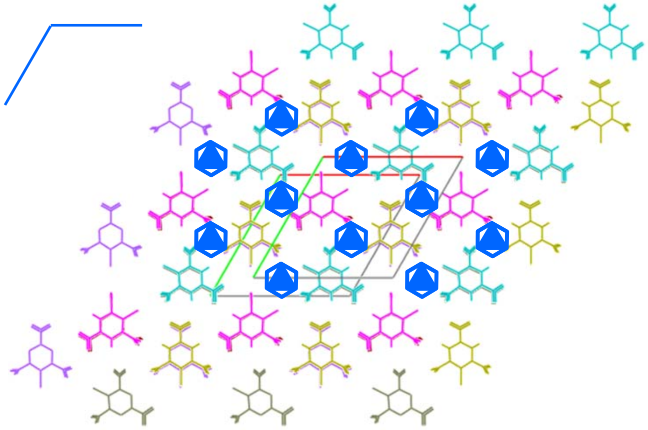


$p\bar{6}$ (#74), z'=1

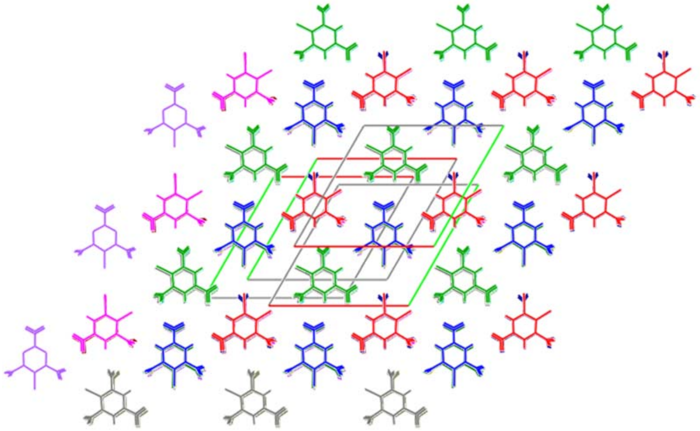
(see also next page)

ZZZVXQ02,
con‘t
($P3_1$, Z’=12)

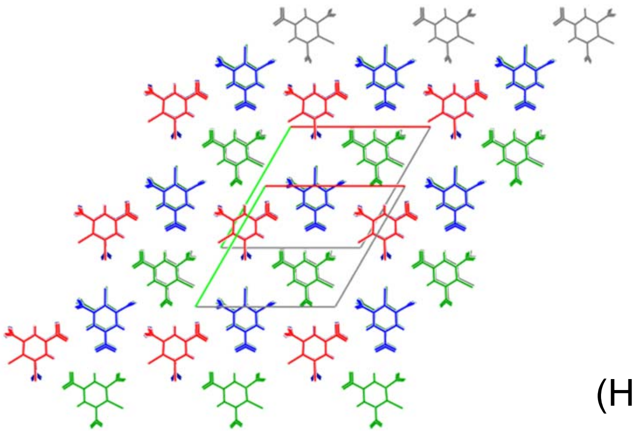
Overlay by translation of layers (001) A1 and A2



Overlay by translation of the four independent layers (001) after inversion of B1 and B2



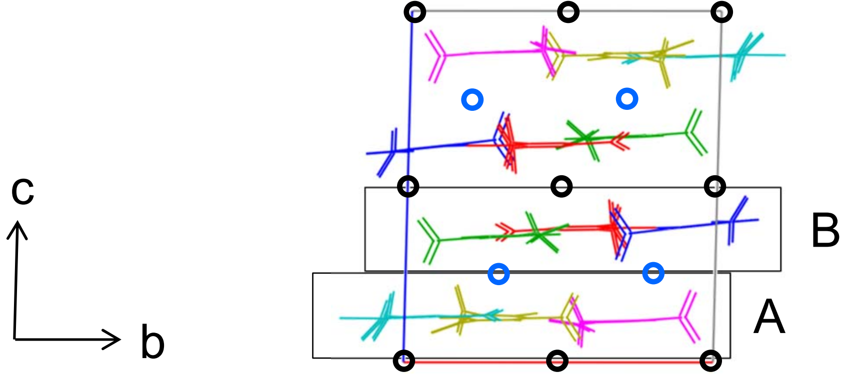
Overlay by translation of layers (001) B1 and B2



(H atoms are shown)

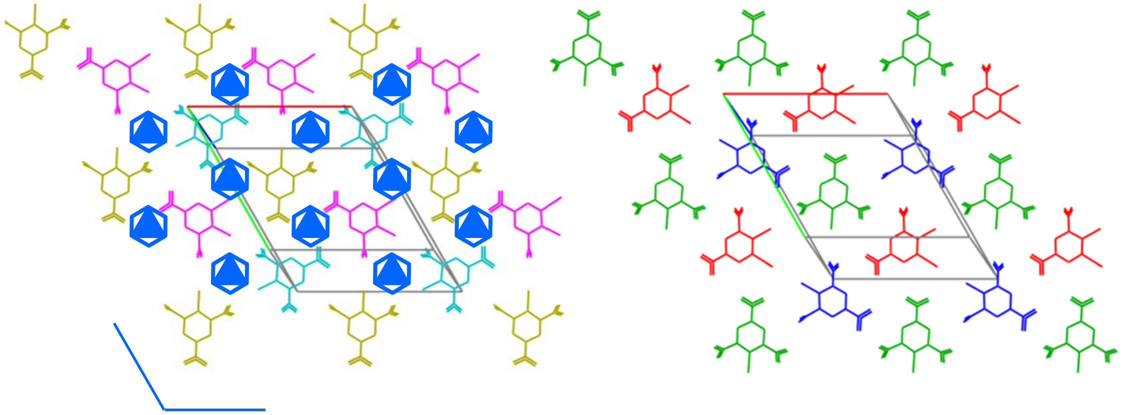
Projection along **a***

ZZZVXQ03
($P\bar{1}$, Z'=6)

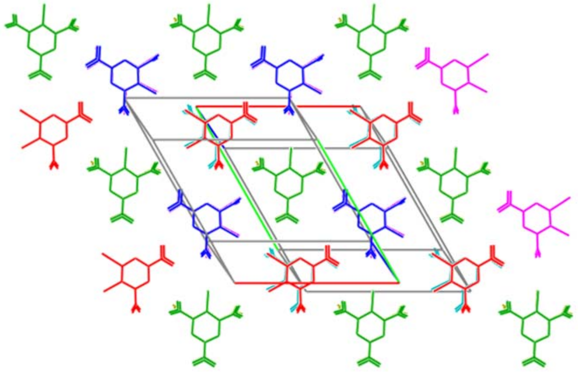


Layers (001) A and B

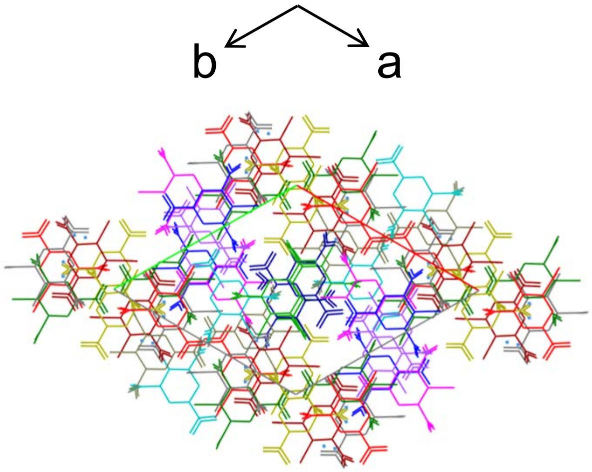
$p\bar{6}$ (#74), z'=1

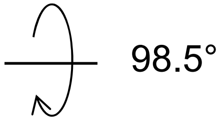


Superposition of A and B
by translation after
inversion of layer B



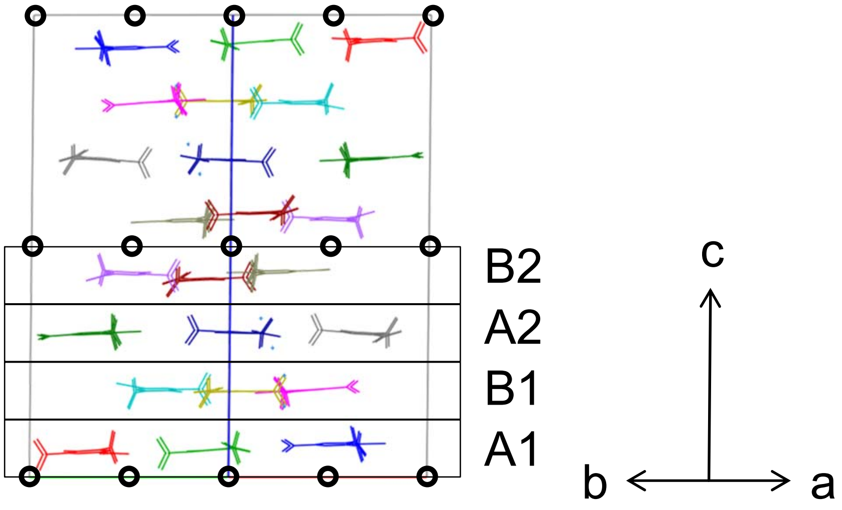
Projection along **c**



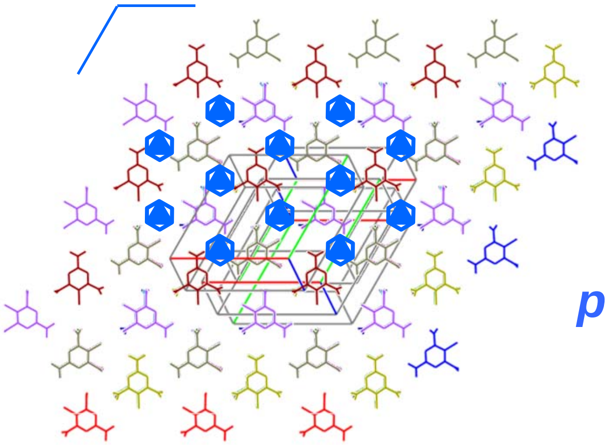


Projection along [110]

ZZZVXQ05
($P\bar{1}$, Z'=12)



Overlay by translation of the four independent layers (001) after rotation of layers B1 and B2 by 180° around the layer normal

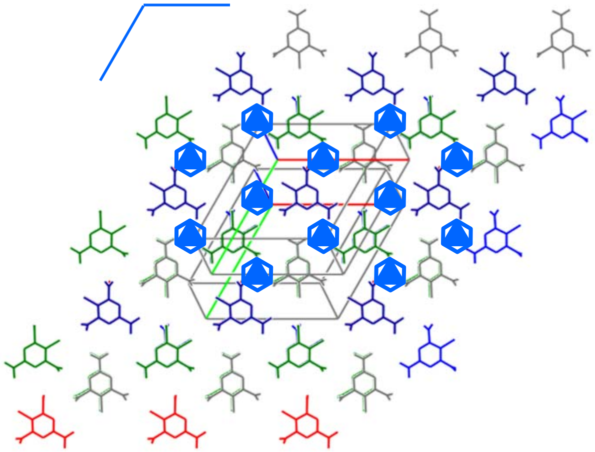


$p\bar{6}$ (#74), z'=1

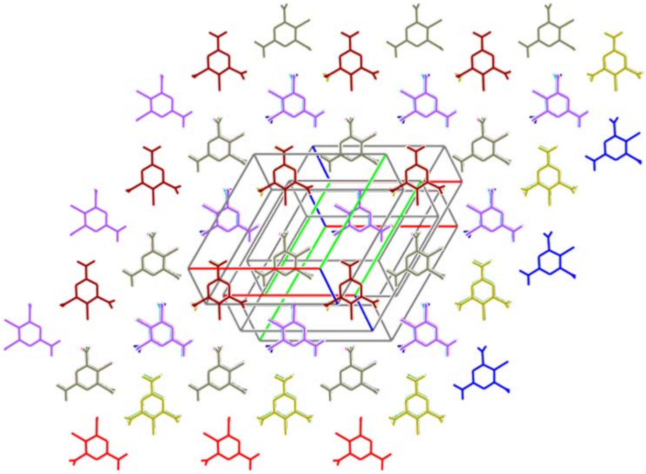
(see also next page)

ZZZVXQ05, con't
($P\bar{1}$, Z'=12)

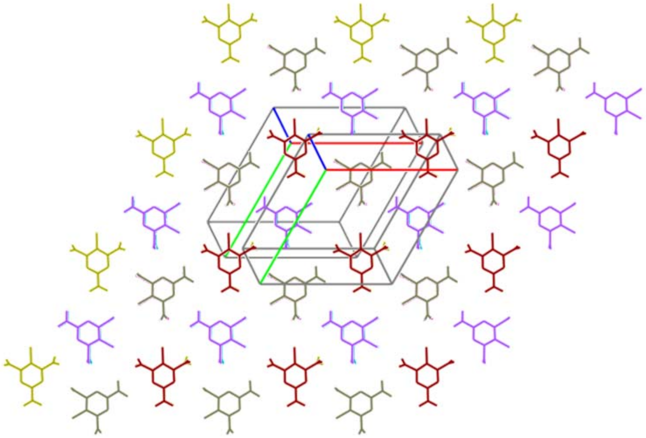
Overlay by translation of layers (001) A1 and A2



Overlay by translation of the four independent layers (001) after inversion of layers B1 and B2

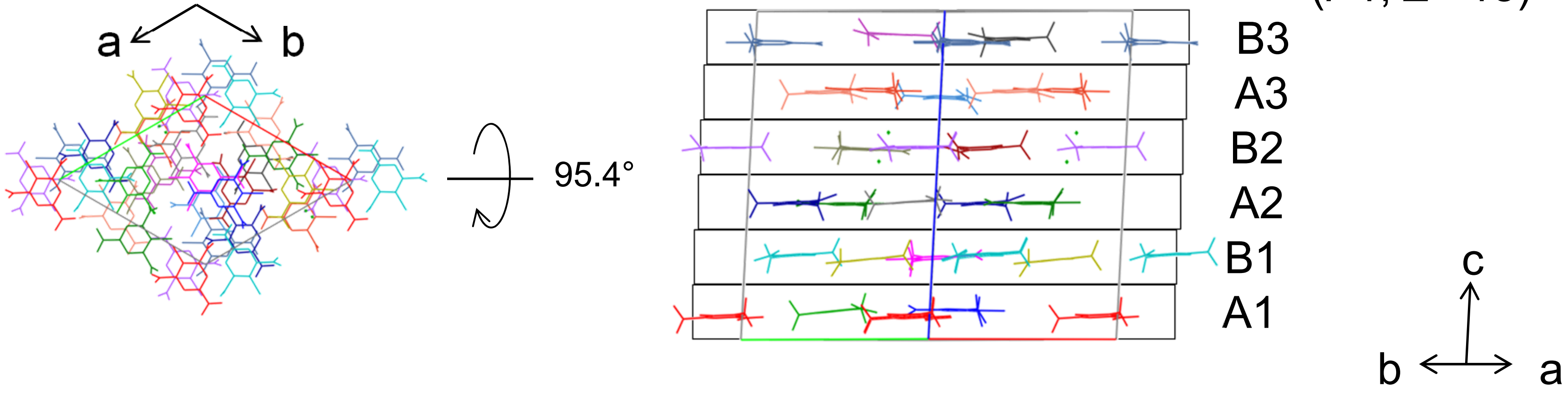


Overlay by translation of layers (001) B1 and B2

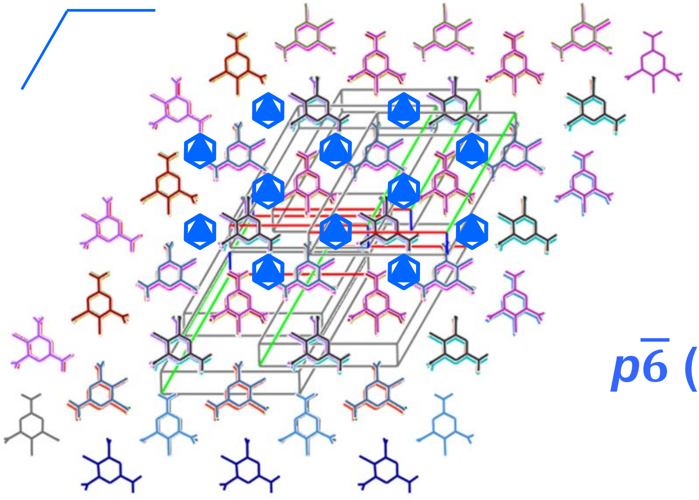


Projection along **c**

ZZZVXQ06
($P1$, Z'=18)



Overlay by translation of the six independent layers (0 0 1) after rotation of layers B1, B2, and B3 by 180° around the layer normal

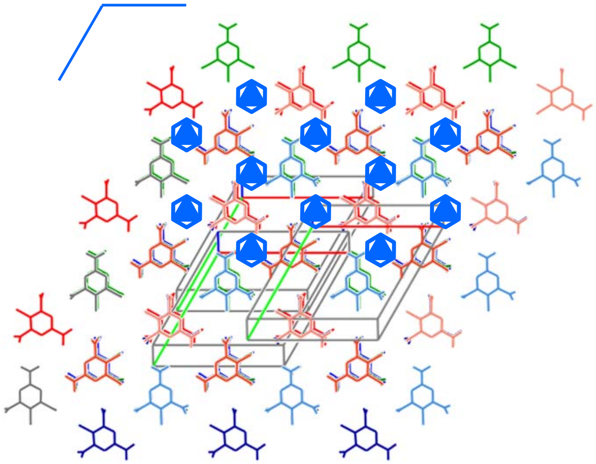


$p\bar{6}$ (#74), z'=1

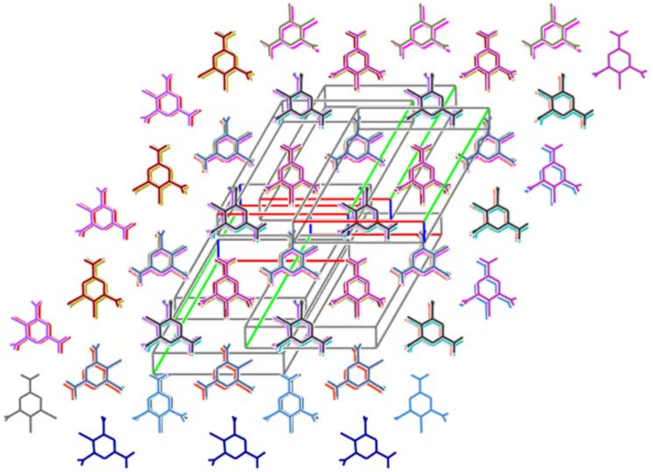
(see also next page)

ZZZVXQ06,
con’t
($P1$, Z'=18)

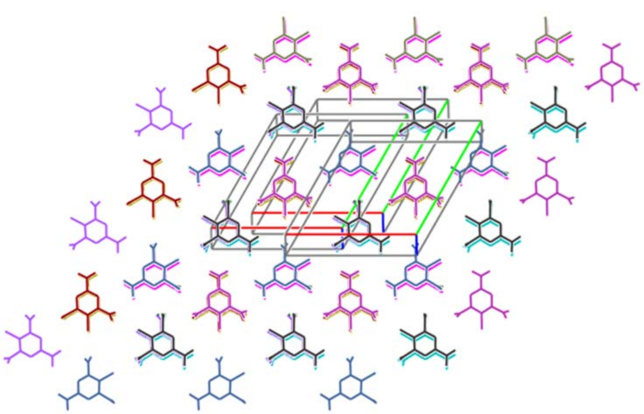
Overlay by translation of layers (001) A1, A2 and A3



Overlay by translation of the six independent layers (001) after inversion of B1, B2 and B3

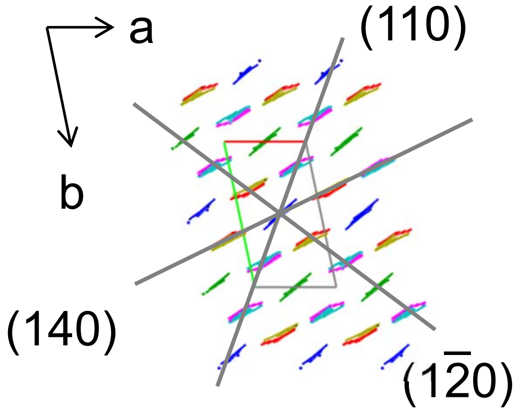


Overlay by translation of layers (001) B1, B2 and B3

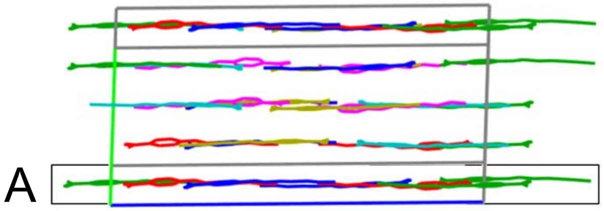


Projections along **c**, $[4\bar{1}0]$, [210] and $[1\bar{1}0]$ showing layers (001), (140), $(1\bar{2}0)$ and (110)

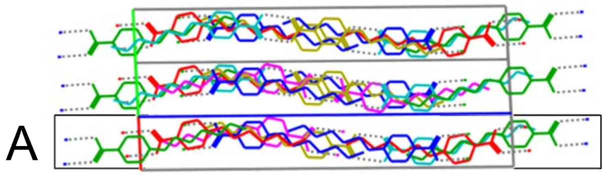
ZZZZCA03
($P\bar{1}$, Z'=6)



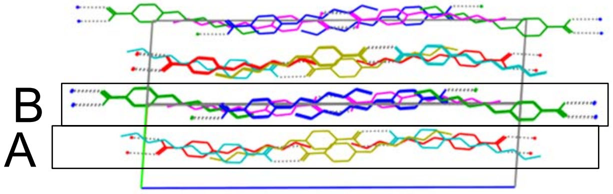
Layers (140)



Layers $(1\bar{2}0)$

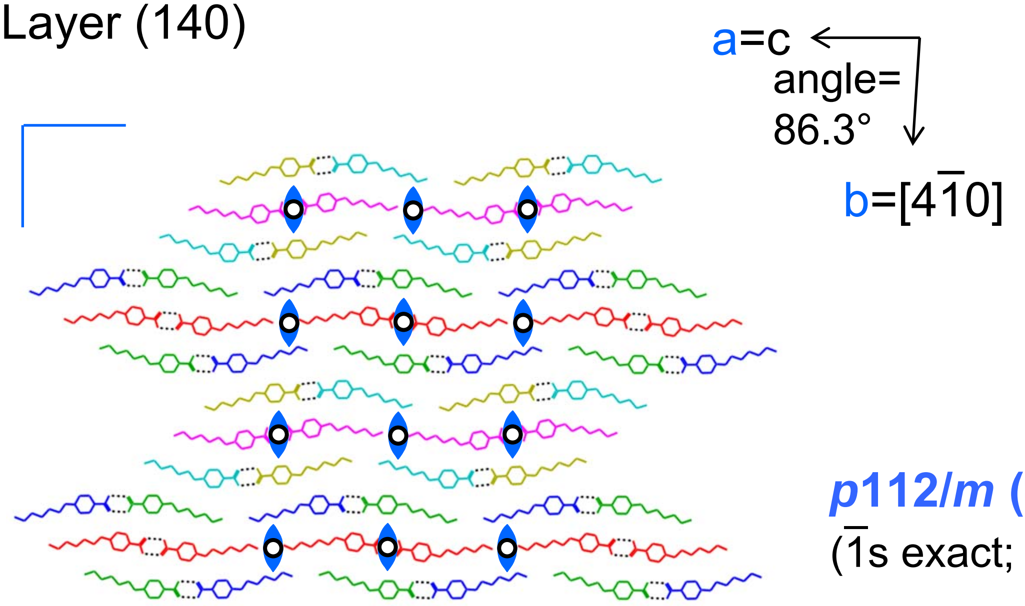


Layers (110)



[the layers $(1\bar{2}0)$ and (110) are less convincing than layer (140)]

Layer (140)

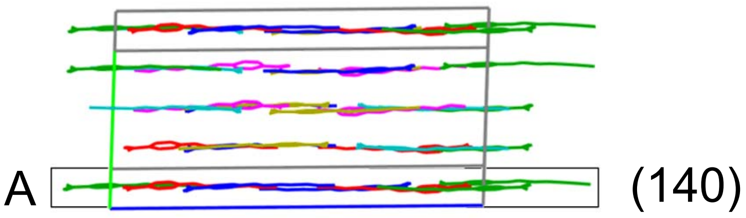


***p112/m* (#6), *z'*=6**

($\bar{1}$s exact; molecules lie on the mirror plane)

ZZZZCA03, con't
($P\bar{1}$, Z'=6)

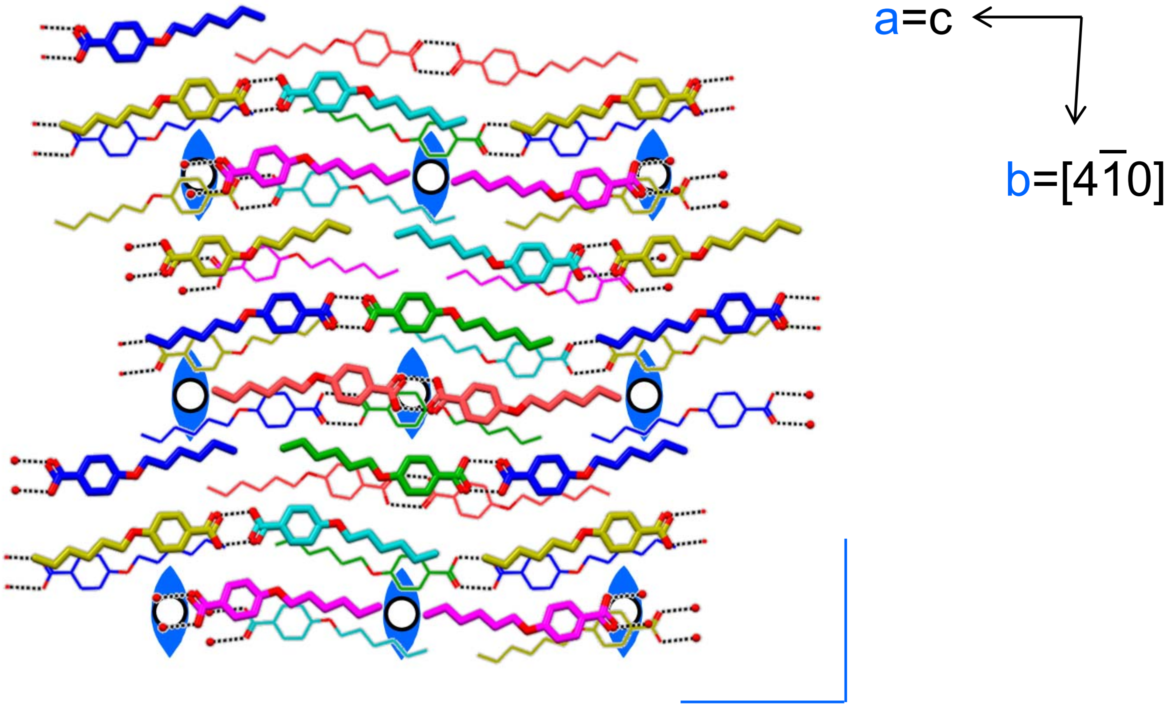
Projection along [4$\bar{1}$0]



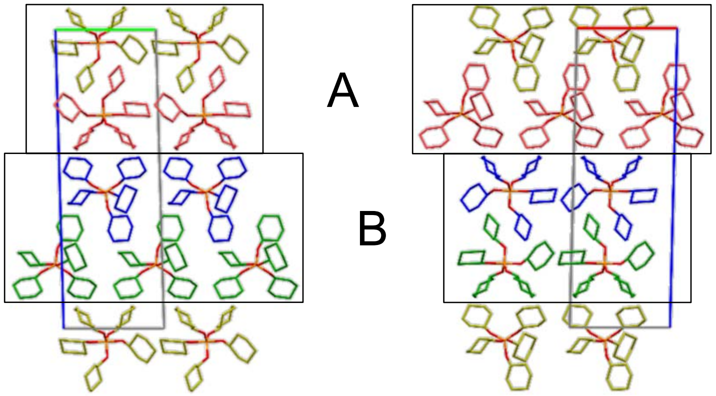
Two adjacent layers (140)

***p*112/*m* (#6), *z'*=6**
($\bar{1}$s exact;
molecules lie on the mirror plane)

The inversion centers within and between adjacent layers are not related in any simple way

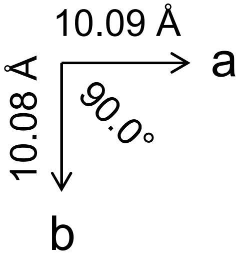


Projections along **a** and **b**

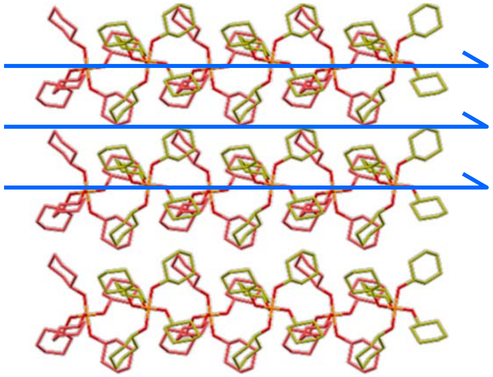


ACEZOX
(*P*1, *Z'*=4)

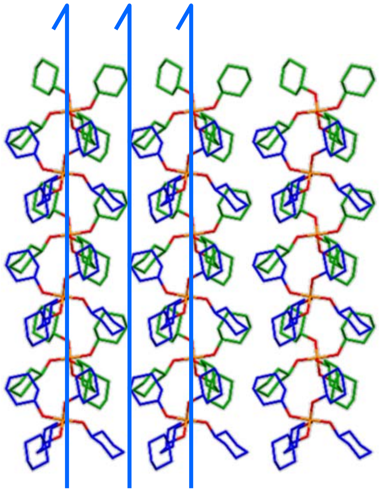
Layers (001) A and B



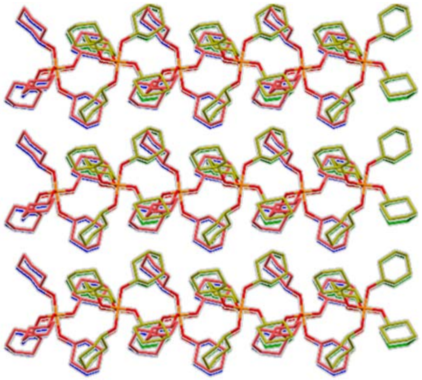
$p2_111$ (#9),
z'=1



$p12_11$ (#9),
z'=1

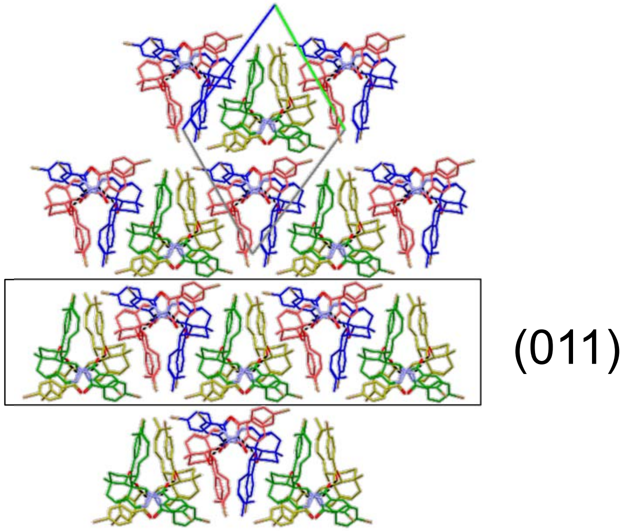


Superposition after rotation of B by 90°around **c*** and then 180° around **a**

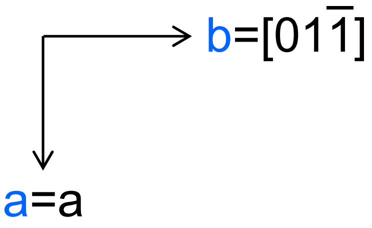


Projection along

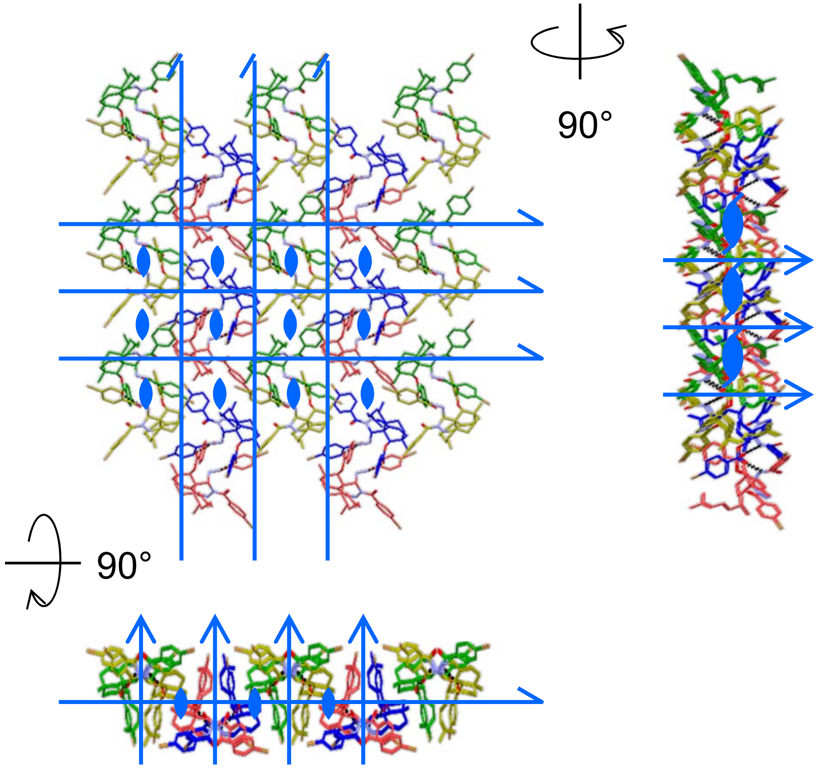
BIHVUJ
(*P*1, *Z'*=4)



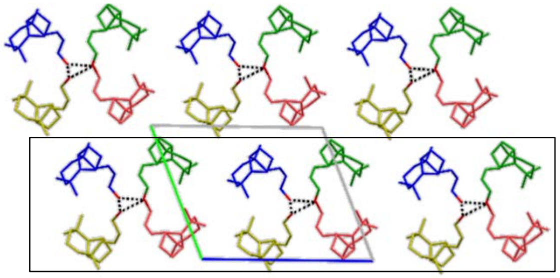
Layer (011)



$p2_12_12$ (#21),
$z'=1$



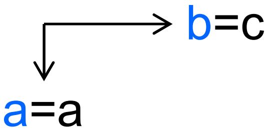
Projection along



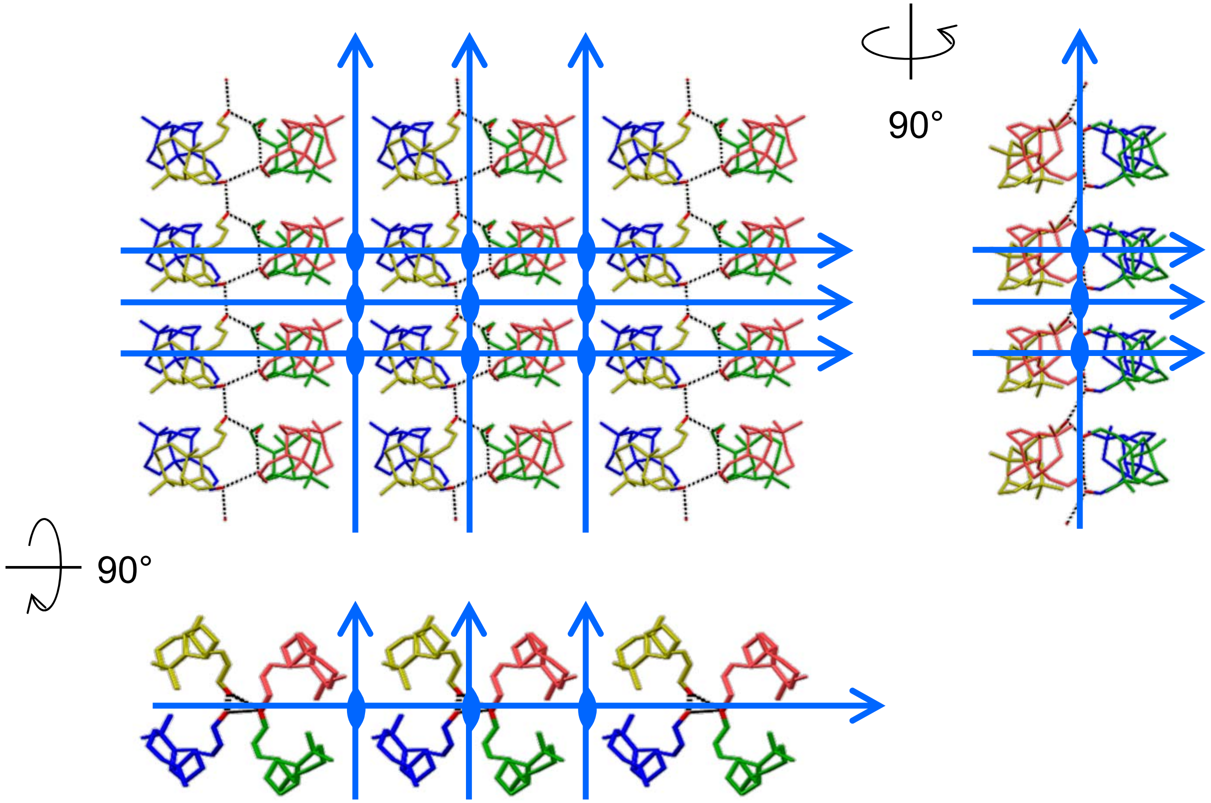
(010)

BIVLIC
($P1$, Z'=4)

Layer (010)

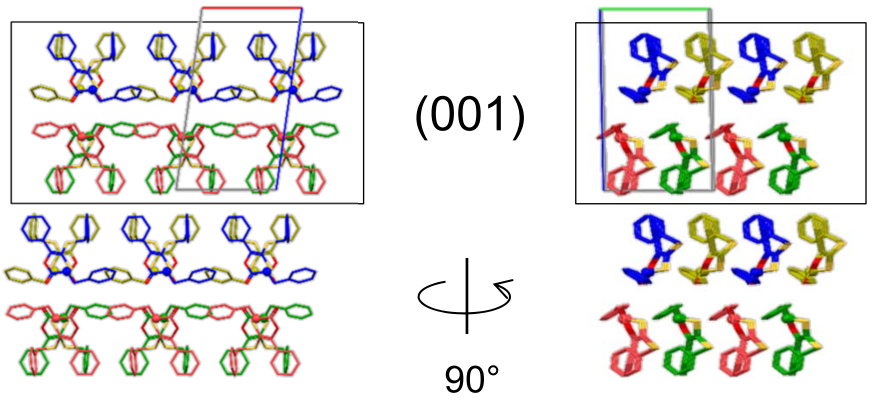


$p222$ (#19),
z'=1

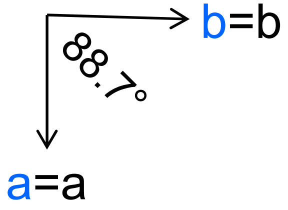


Projections along **b** and after rotation
(γ = 88.7°)

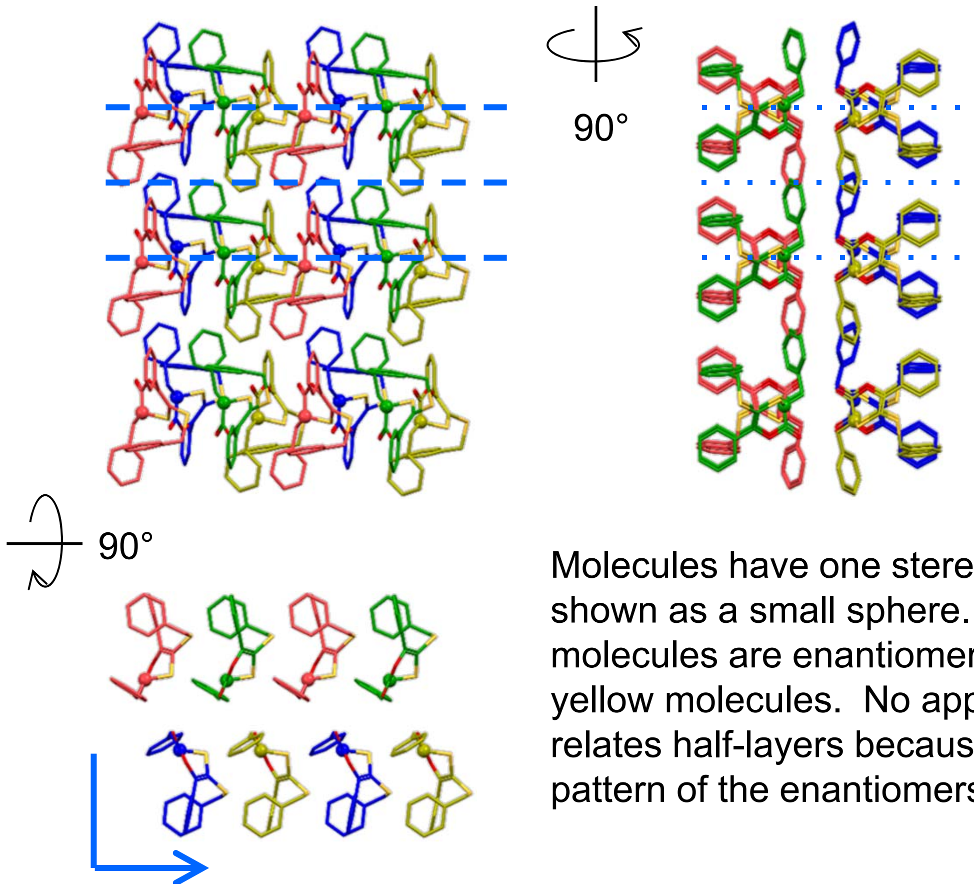
CEHYEW
(*P*1, *Z'*=4)



Layer (001)



***pb*11 (#12),**
***z'*=2**

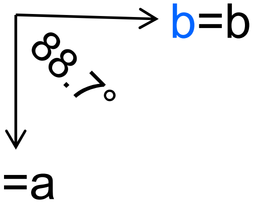


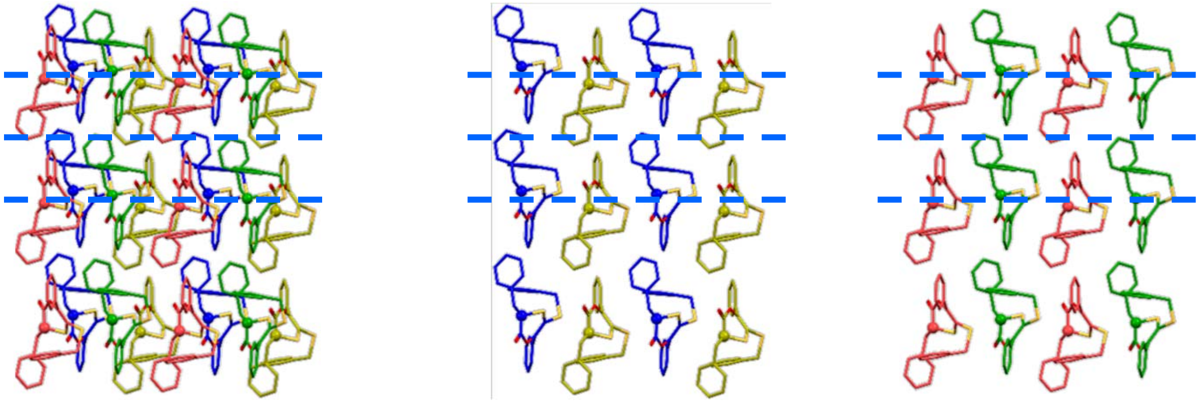
Molecules have one stereocenter, which is shown as a small sphere. Green and red molecules are enantiomers as are blue and yellow molecules. No approximate symmetry relates half-layers because of the alternation pattern of the enantiomers.

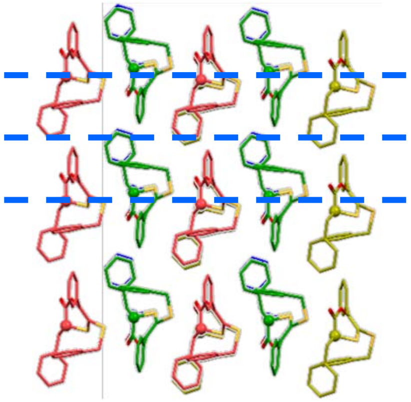
(See also next page)

Layers and half-layers (001) and a superposition of the half-layers by translation of *ca* **b**/4

CEHYEW,
con't
(*P*1, *Z'*=4)

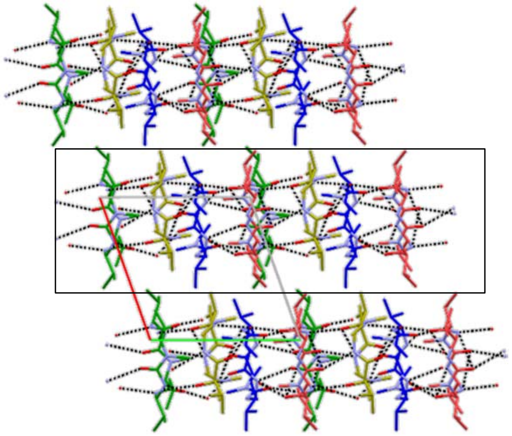






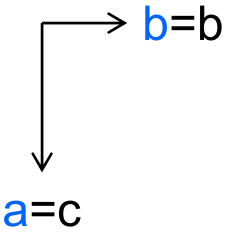
(the superimposed molecules are enantiomers)

Projection along

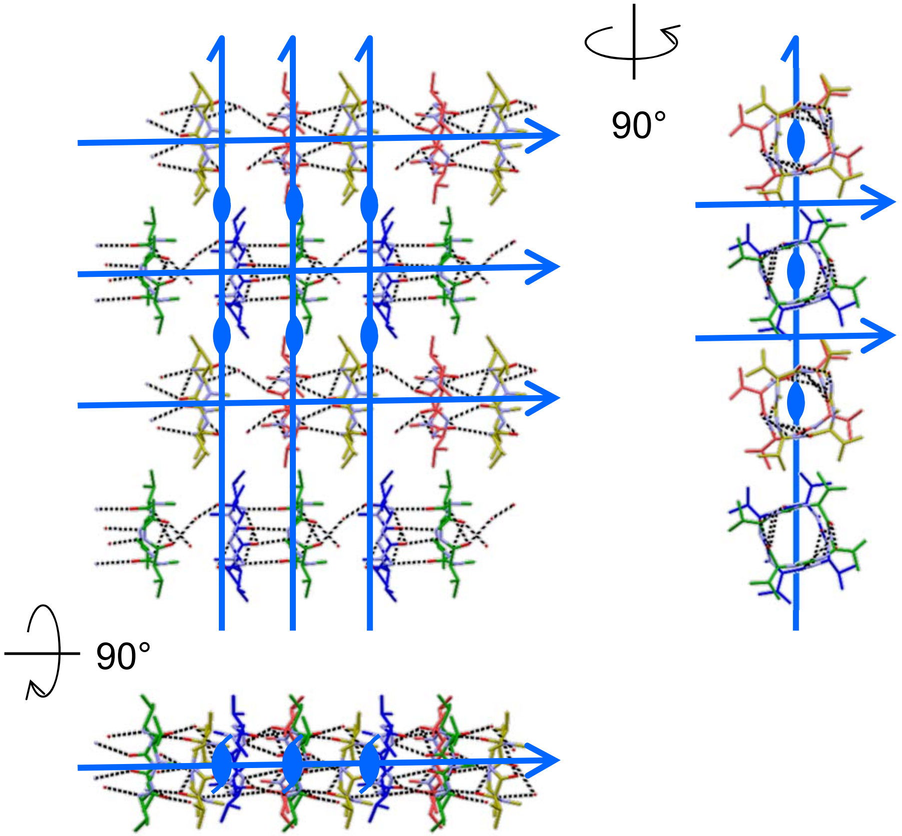


DOVXIW
($P1$, $Z'=2$)

Layer (100)

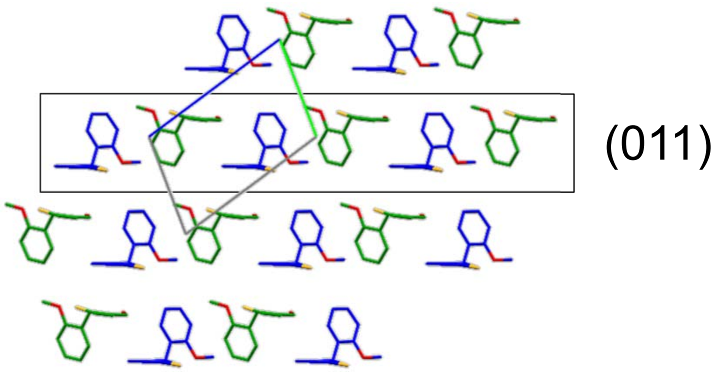


$p2_{1}22$ (#20),
$z'=2=4(½)$



Projection along **a**

DUNHAW
($P1$, $Z'=2$)

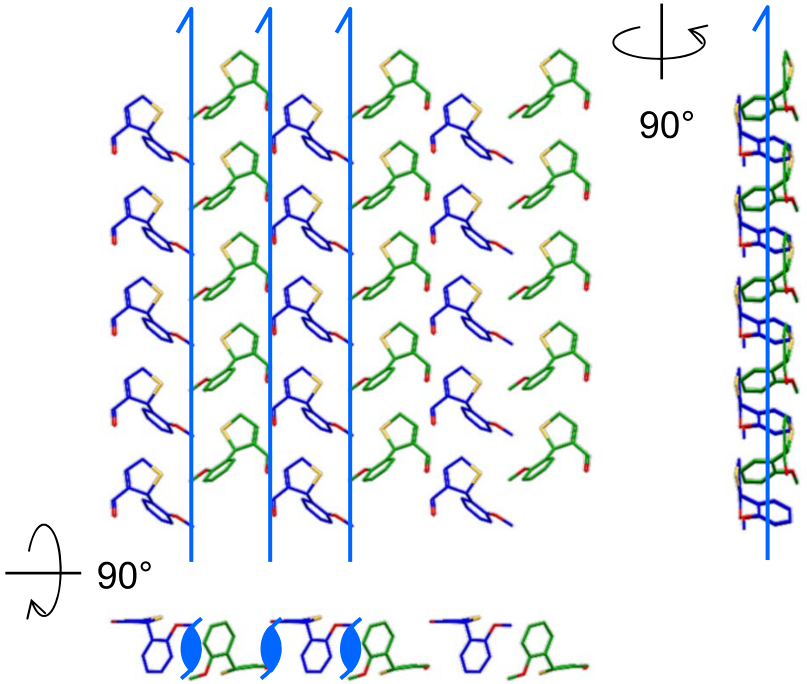


Layer (011)

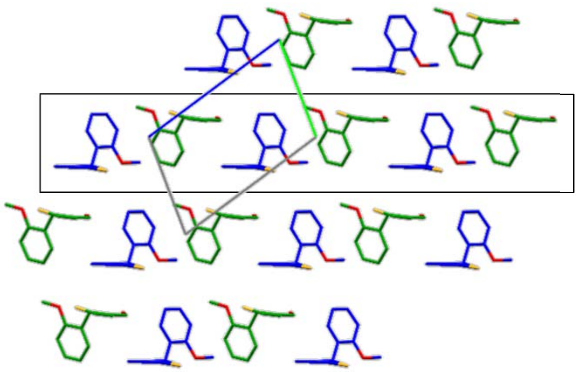
$b=[01\bar{1}]$

$a=a$

$p2_111$ (#9),
$z'=1$

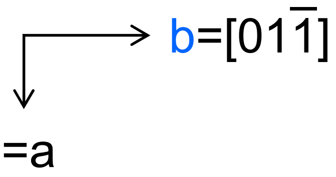


Projection along **a**

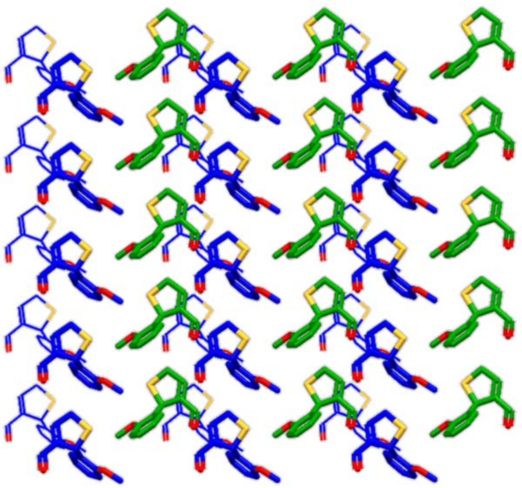


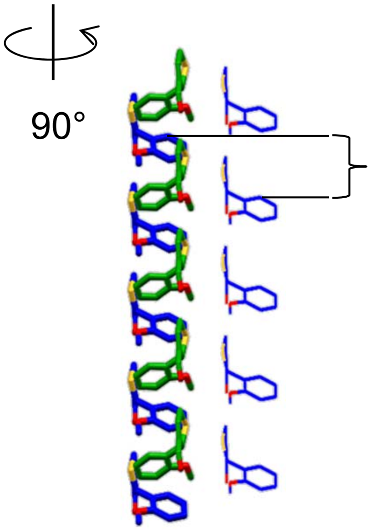
DUNHAW, con't
($P1$, $Z'=2$)

1.5 layers (011)

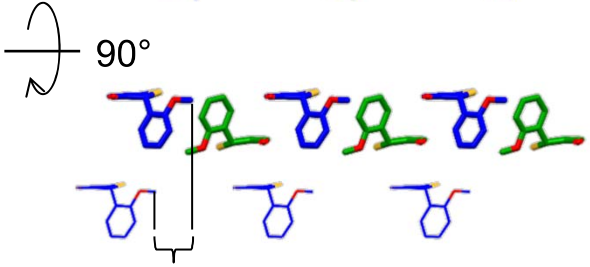


$p2_111$ (#9),
$z'=1$





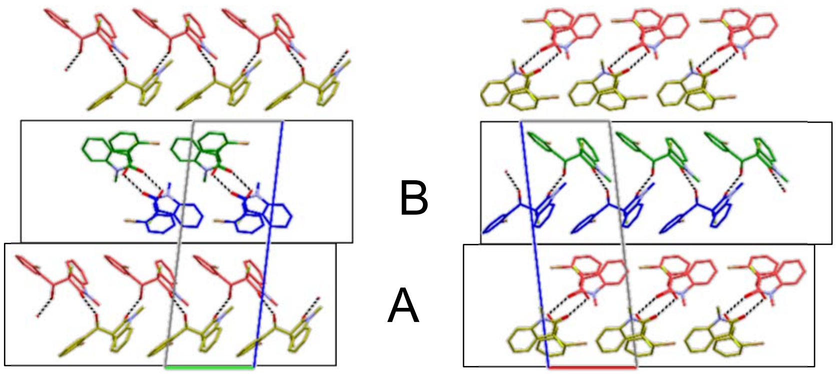
If the 2_1 along **a** is not confined to the layer then adjacent layers must be aligned along **a**



An offset along **b** has no signifycance because in 3-D the corresponding angle would be β, which can have any value

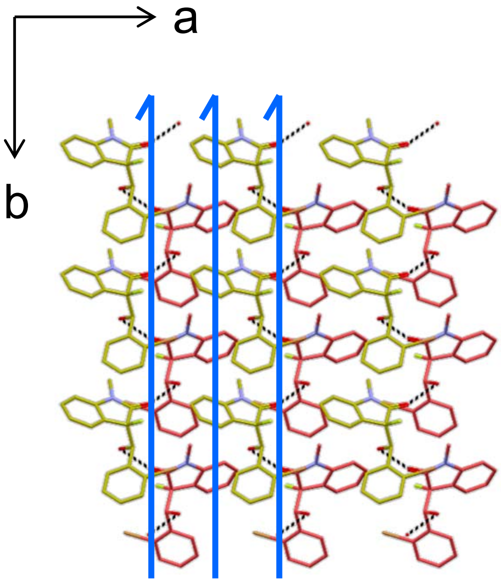
Projections along
a and **b**

a = 7.99 Å
b = 8.05 Å
γ = 90.01°

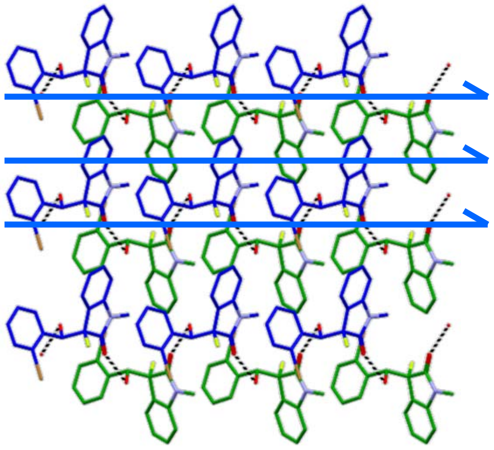


ECEHAY
($P1$, Z'=4)

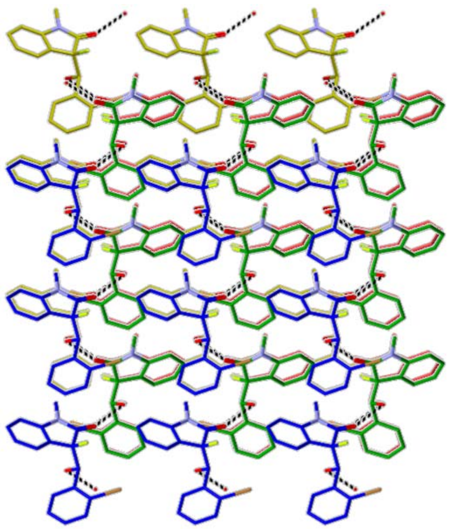
Layers (001) A and B, and their superposition after rotation of B by 90°



$p12_11$ (#9),
z'=1

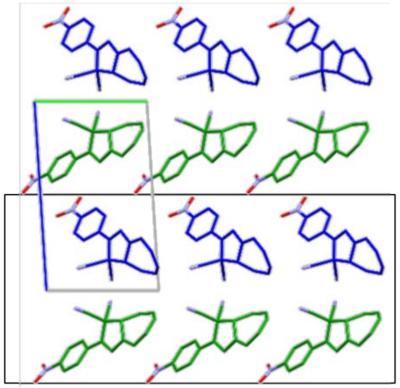


$p2_111$ (#9),
z'=1



Projection along **a**

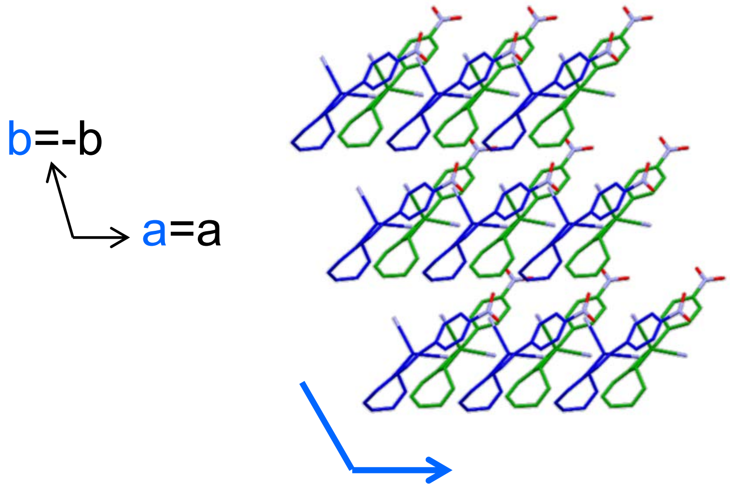
FIVPOR
(*P*1, *Z'*=2)



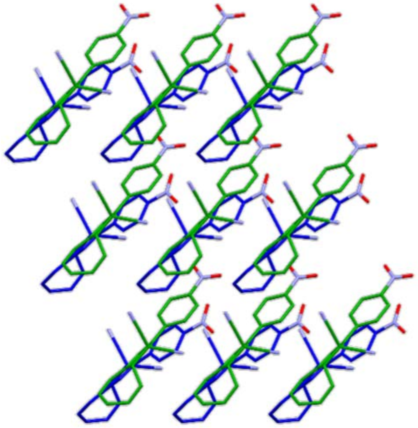
The two molecules are separable enantiomers that also differ in the rotation of the 4-nitrophenyl substituent

Layer (001)

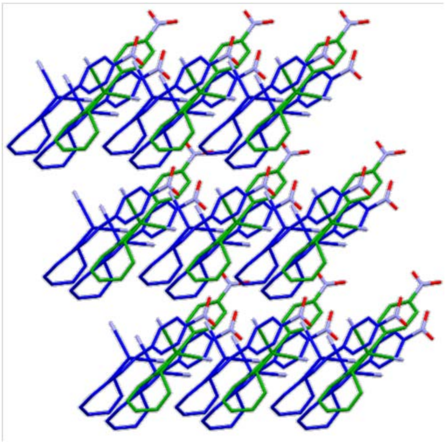
***p*11*a* (#5), *z'*=1**



0.5<*z*<1.5
good approximate *a* glide

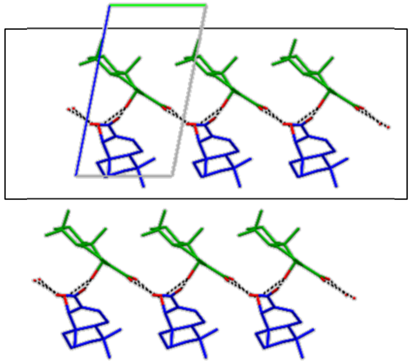


0.0<*z*<1.0
no approximate symmetry



0.0<*z*<1.5
showing offset between layers

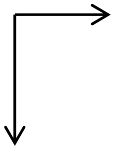
Projection along **a**



(001)

FUZTIE
(P1, Z'=2)

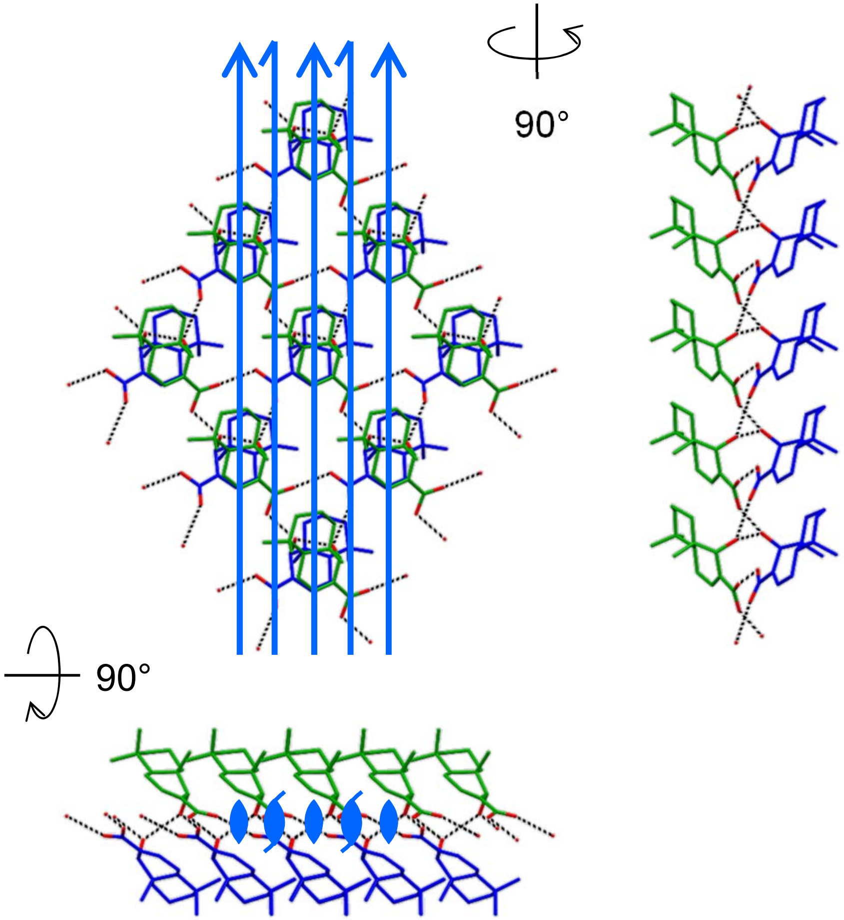
Layer (001)



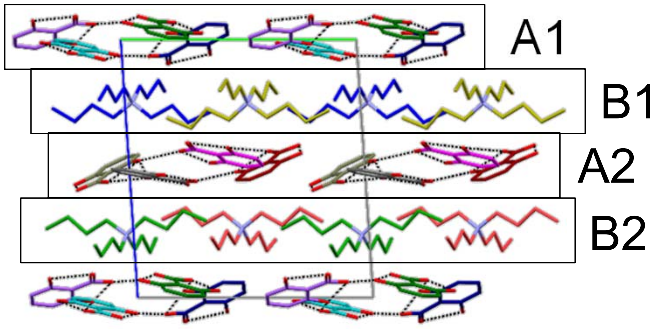
b=[110]

a=[$\bar{1}$10]

***c*211 (#10),**
***z'*=1**



Projection along **a**

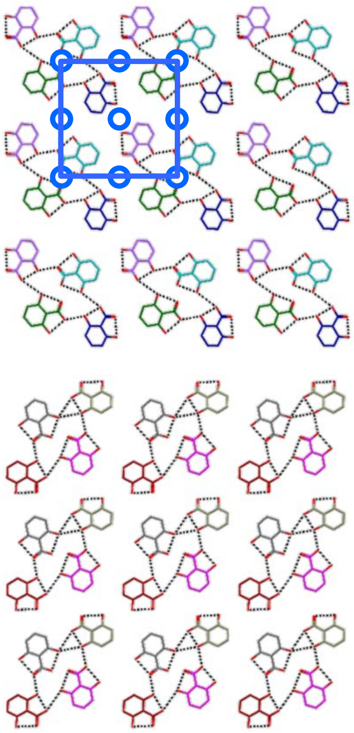


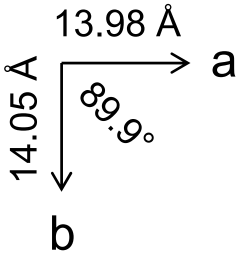
HUZDOV
($P1$, Z'=4)

$Bu_4N^+ A^-$ **.** A, where A is
2,6-dihydroxybenzoic acid

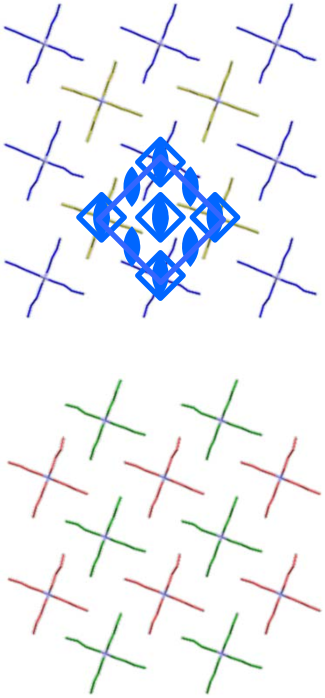
Layers (001) A1, A2 (A^-, A pairs) and B1, B2 (cations)

***$p\bar{1}$* (#2),**
***z'*=1**
(for an A^-,
A pair)



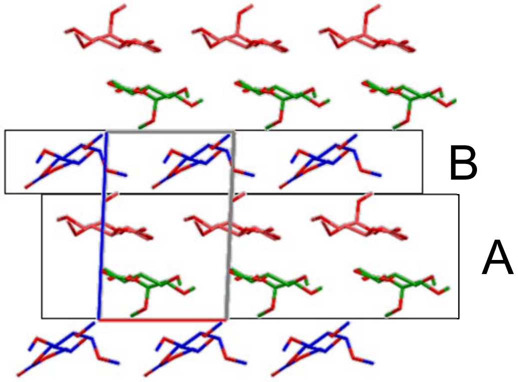


***$p\bar{4}$* (#50),**
***z'*=1/4**



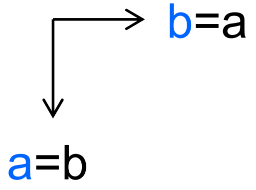
pseudo
translations
[110]/2, [1$\bar{1}$0]/2

Projection along **b**

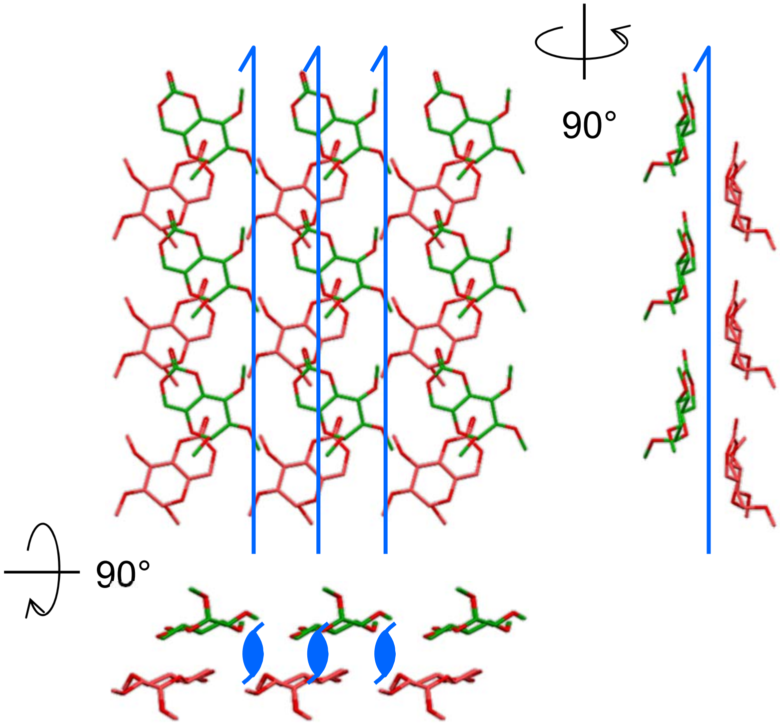


IFAFUS
($P1$, Z'=3)

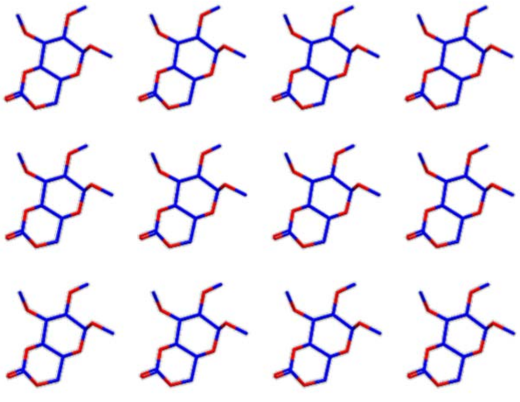
Layers (001) A and B



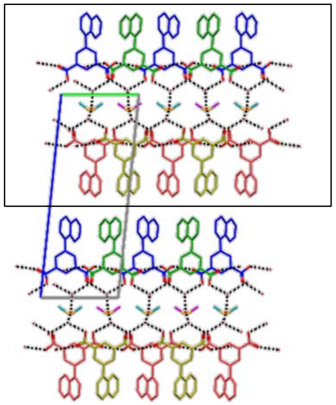
$p2_1 11$ (#9),
z'=1



$p1$ (#1),
z'=1



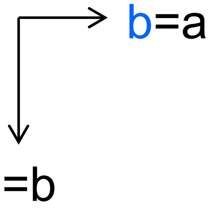
Projection along **a**



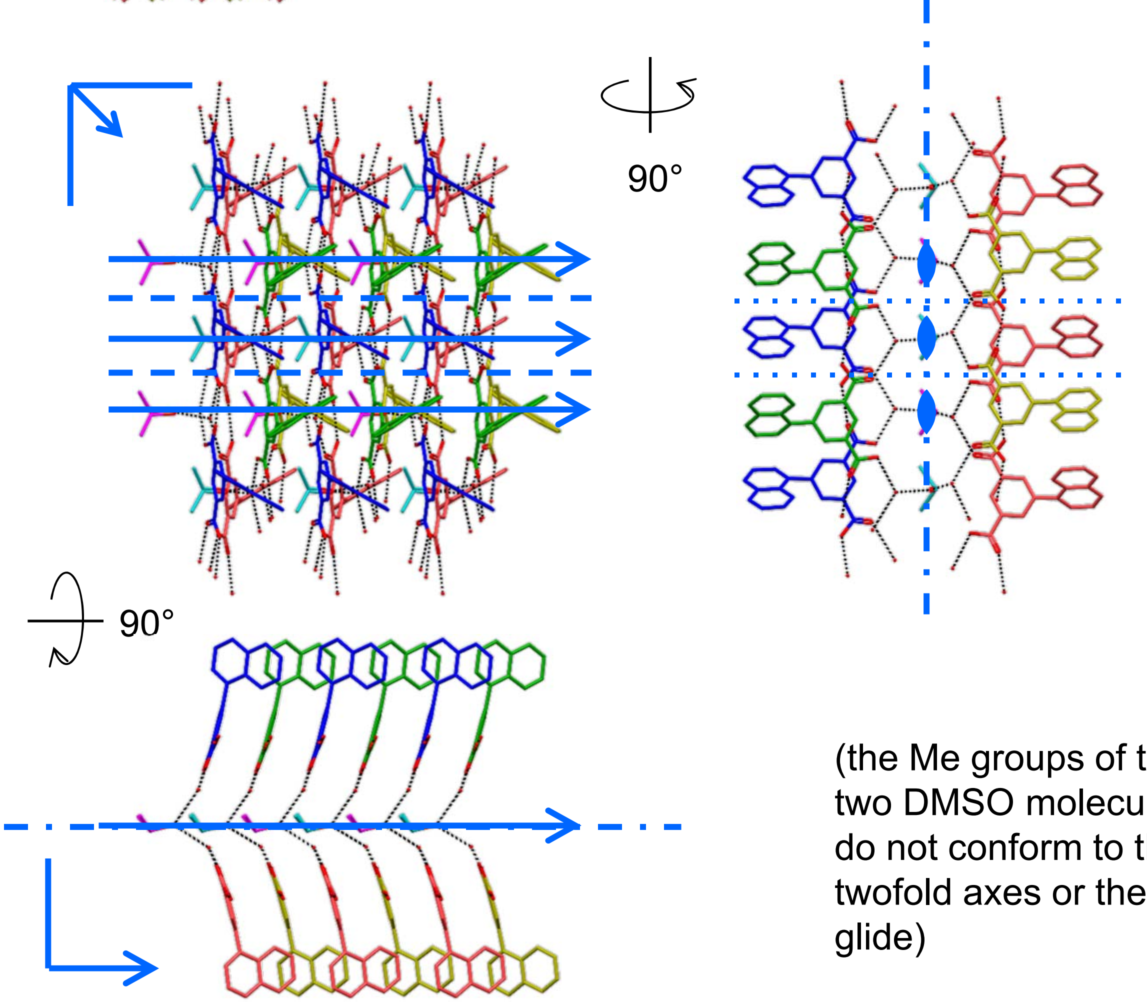
(001)

IGARIT
($P1$, Z'=2)
(a 2:1:2 DMSO, H_2O solvate)

Layer (001)



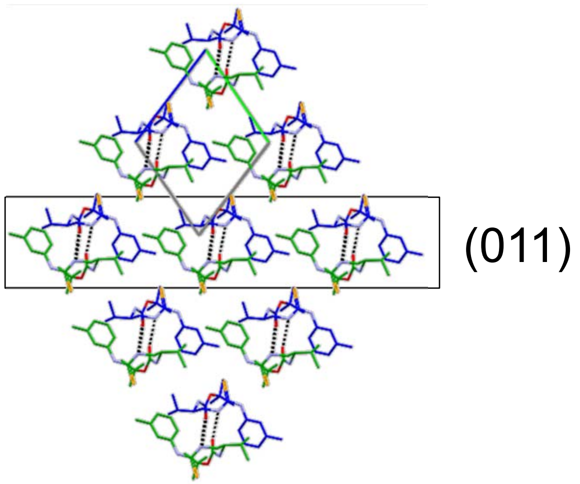
***pb2n* (#34),**
***z'*=1**



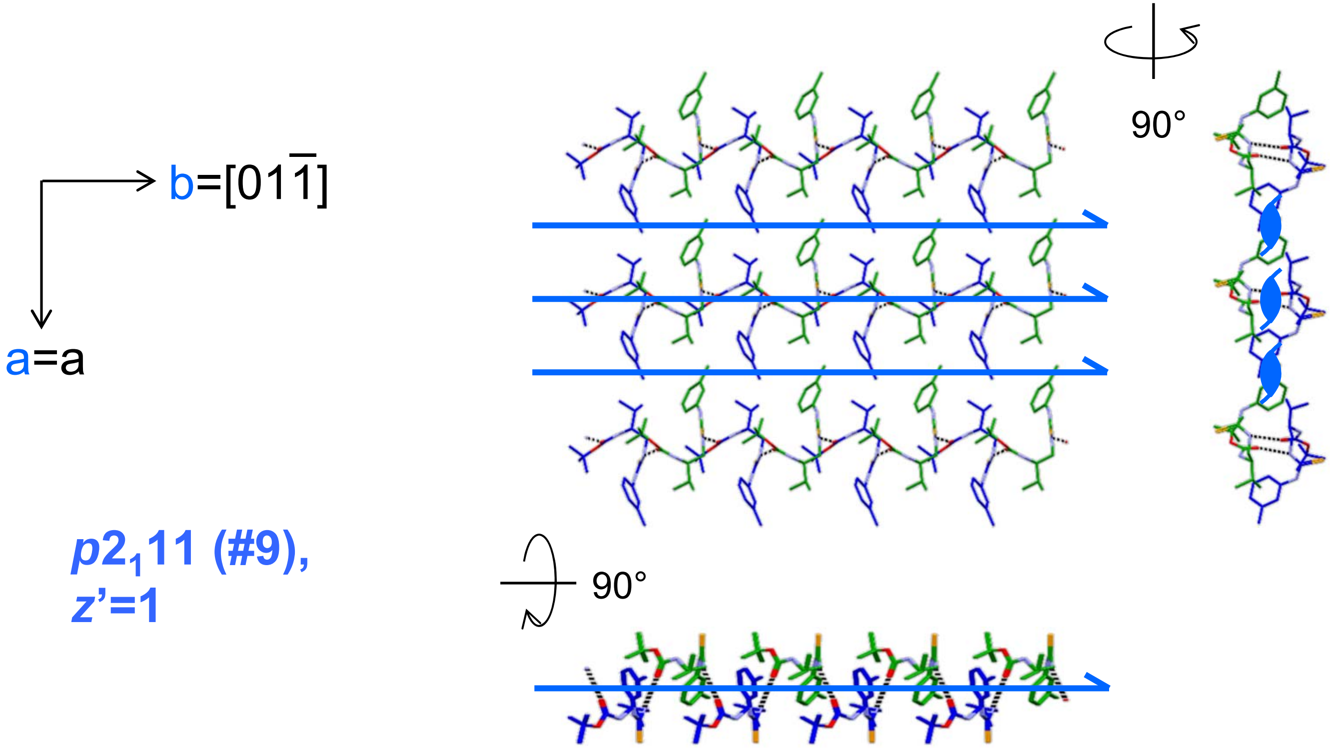
(the Me groups of the two DMSO molecules do not conform to the twofold axes or the *n* glide)

Projection along **a**

INAGAH
($P1$, Z'=2)



Layer (011)

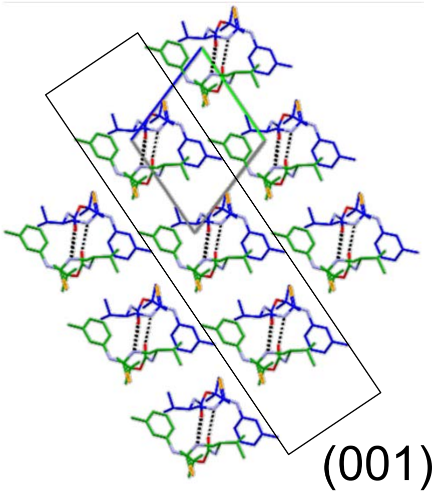


$p2_111$ (#9),
z'=1

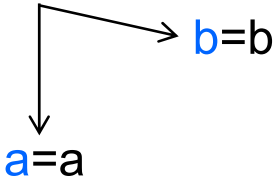
INAGAH, con't (*P*1, *Z'*=2)

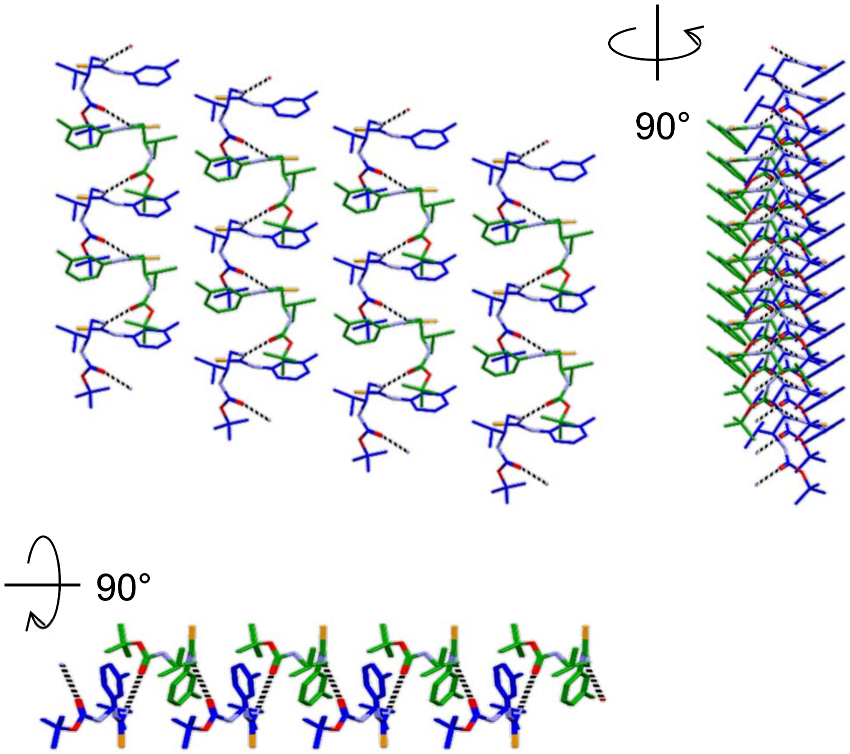
Projection along **a**

layer (001) is a less good choice than (011)



Layer (001)



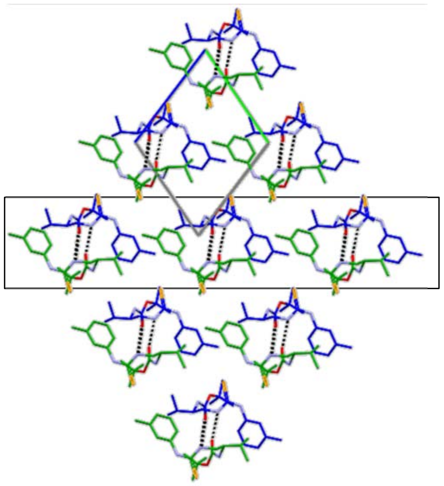


p1 (#1), z'=2

(001) has simpler indices than (011) and the approx.-imate 2_1 axis along **a** is visible but there is no approximate 2-D symmetry because there is no approx.-imate translation approximately perpendicular to **a**

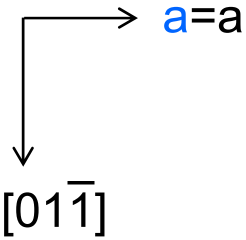
Projection along **a**

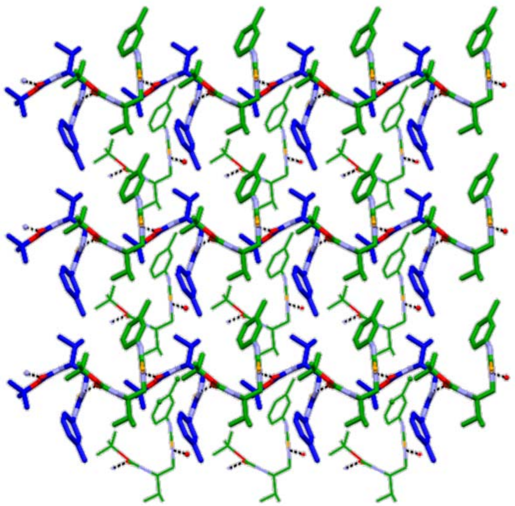
INAGAH,
yet again
($P1$, Z'=2)

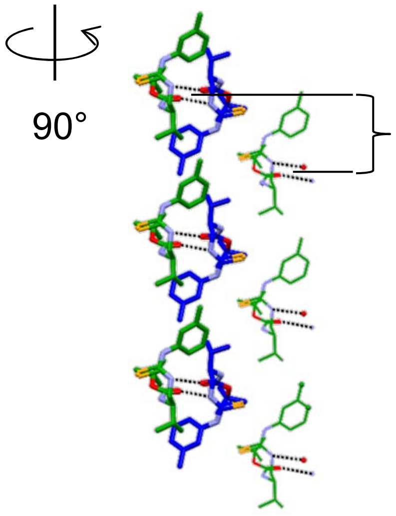


1½ layers (011)

(the half layer is drawn
with thinner lines)

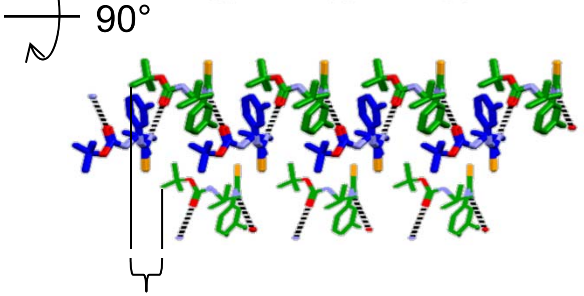






An offset along
b has no
signifycance
because in 3-D
the corre-
sponding angle
would be β,
which can have
any value

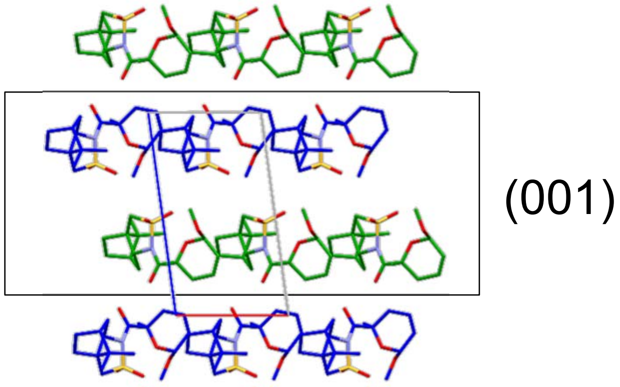
***p*2₁11 (#9),**



If the 2_1 along **a** is not
confined to the layer then
adjacent layers cannot be
offset along **a**

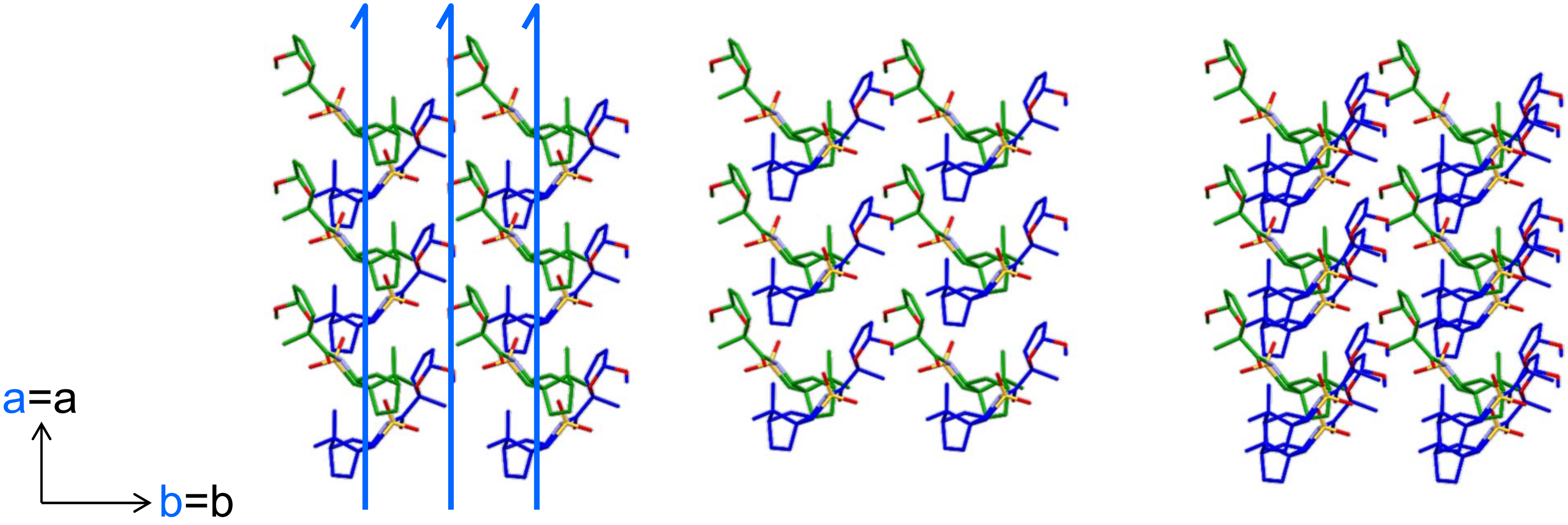
Projection along **b**

JAVKOG
($P1$, $Z'=2$)



Layer (001)

$p2_111$ (#9), $z'=1$

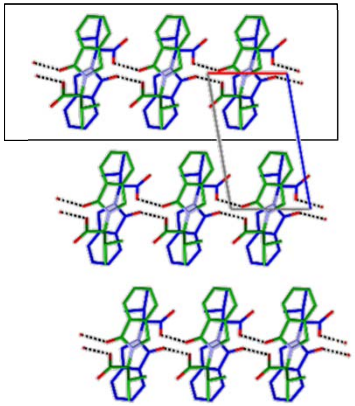


$0.1<z<1.1$
good approximate 2_1 axes

$-0.4<z<0.6$
spacing along **a** is neither ~0 nor ~½

$-0.4<z<1.1$
showing offset between layers along **a**

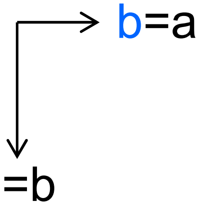
Projection along **b**



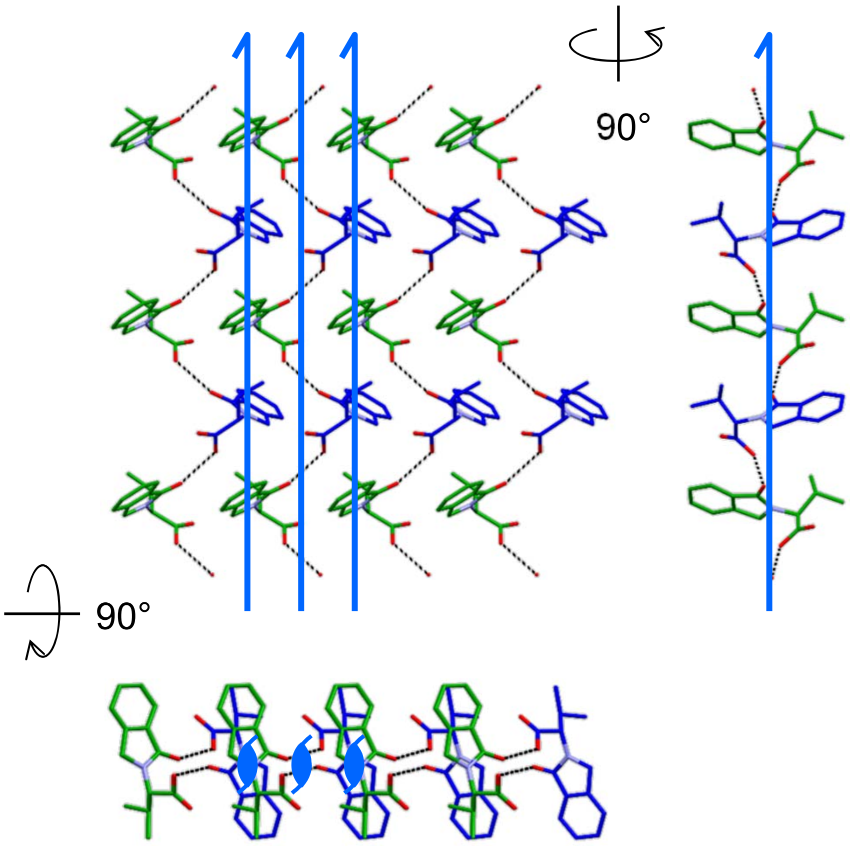
(001)

KOPVEQ
($P1$, $Z'=2$)

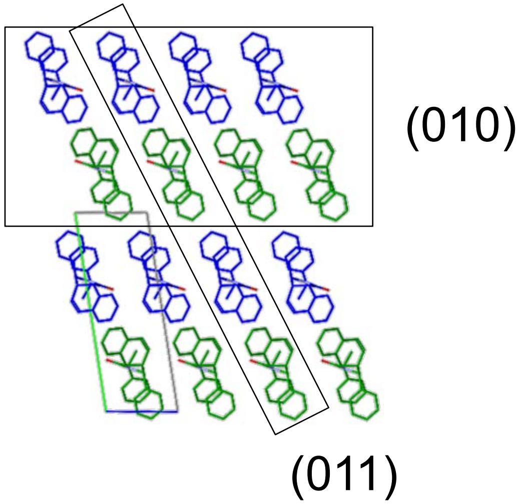
Layer (001)



$p2_111$ (#9),
$z'=1$



Projection along

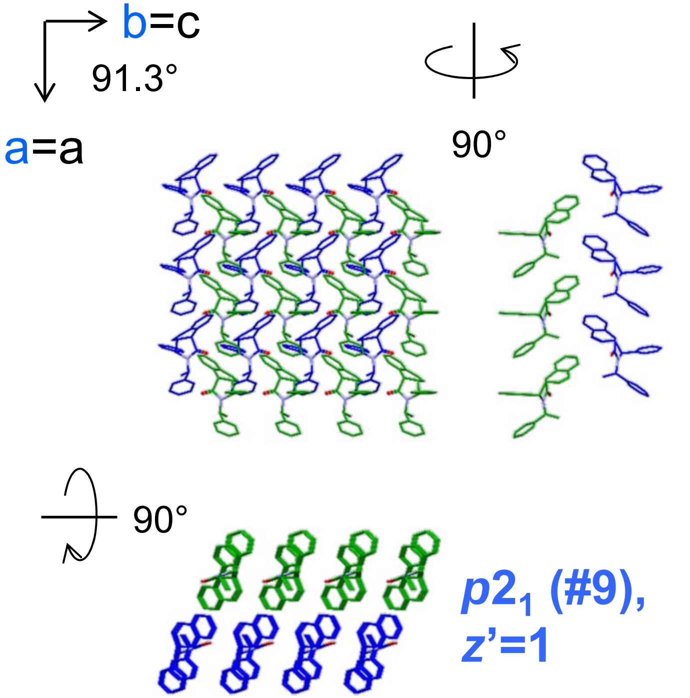


MILCOZ
($P1$, Z'=2)

Layers (011) are better separated than layers (010) but have less 2-D approximate symmetry because there is no simple translation approximately perpendicular to **a**.

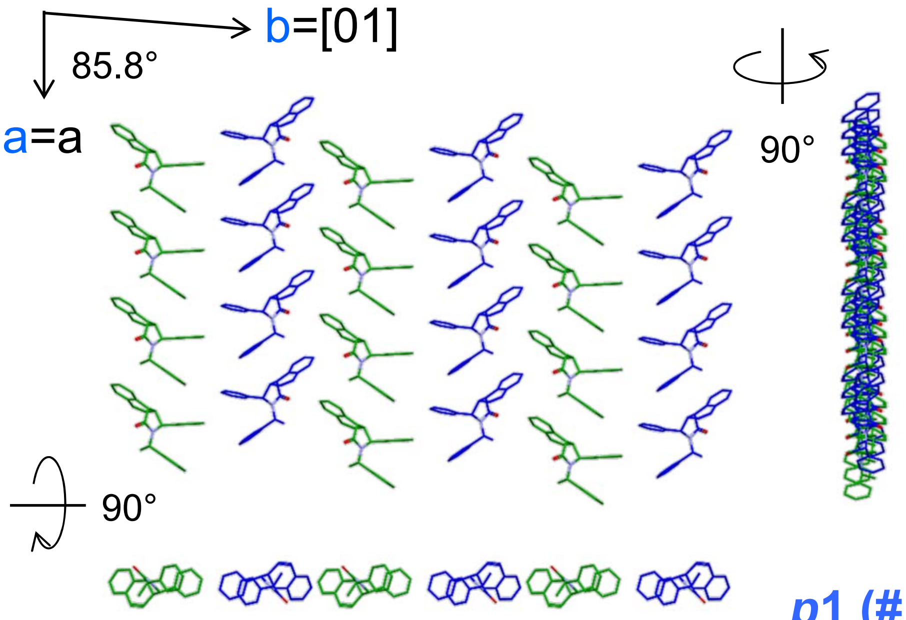
Layers (010) and (011)

(010):



***p*2$_1$ (#9), *z*'=1**

(011):

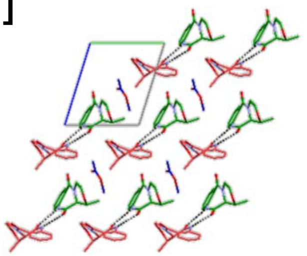


***p*1 (#1), *z*'=*z*=2**

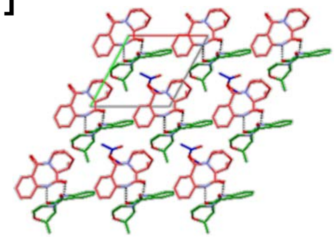
Projections along various directions

NUKQEQ
($P1$, Z'=2)

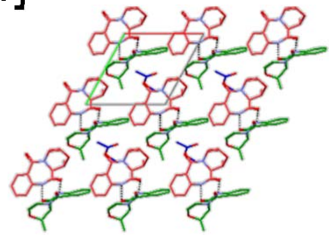
[100]



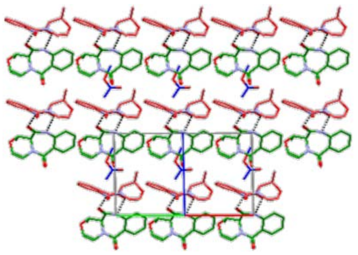
[010]



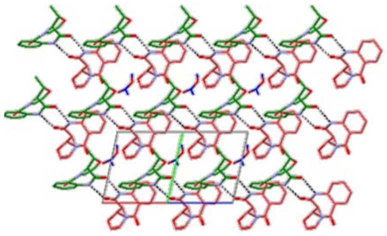
[001]



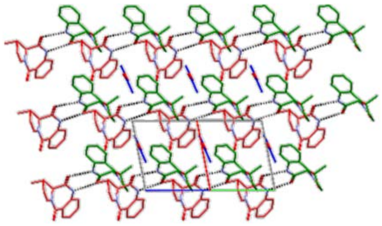
[110]



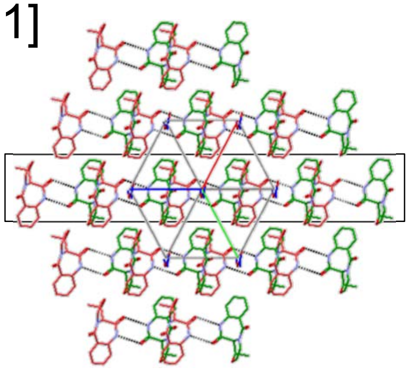
[101]



[011]



[111]



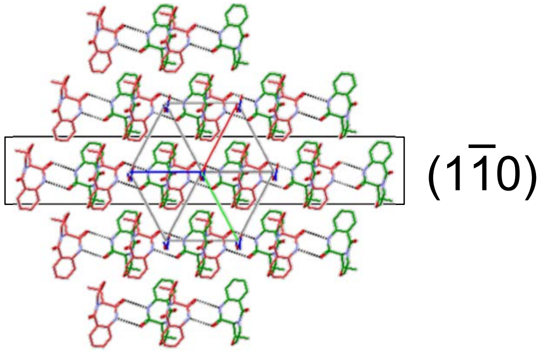
($1\bar{1}0$)

Various layer descriptions are possible but only one layer has extra approximate symmetry

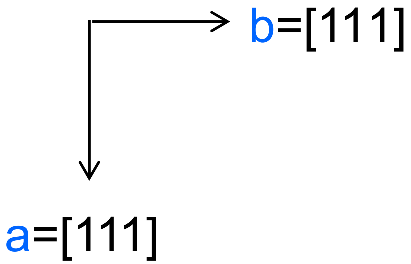
(see next page)

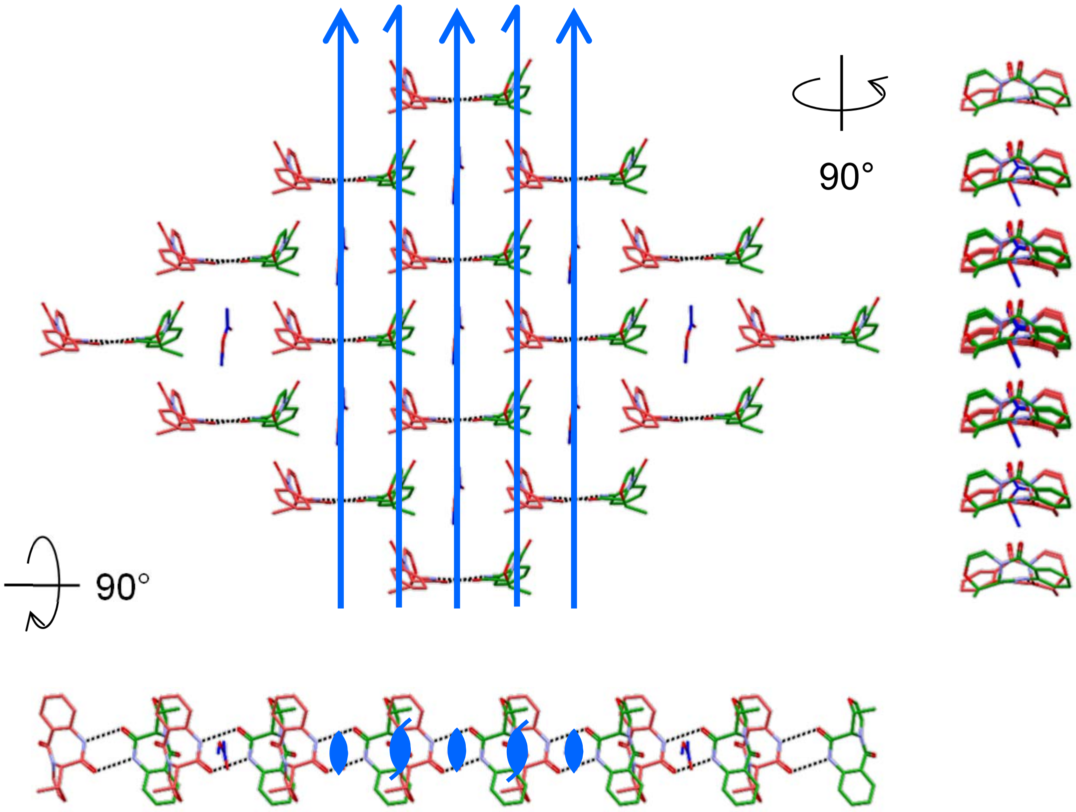
NUKQEQ,
con't
(*P*1, *Z'*=2)

Projection along [111]



Layer $(1\bar{1}0)$



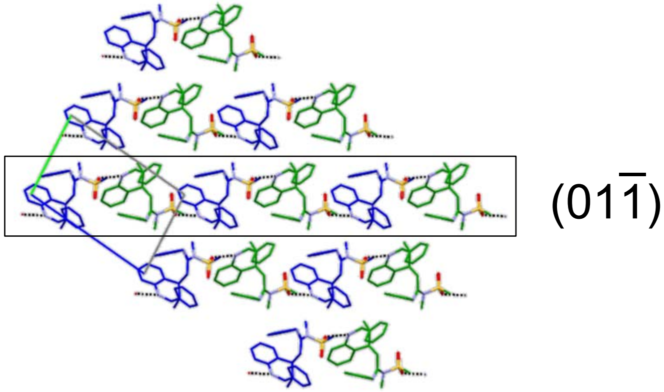


***c*211 (#10),**
***z'*=1**

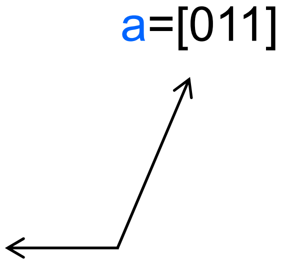
(included
solvent would
have to be
disordered)

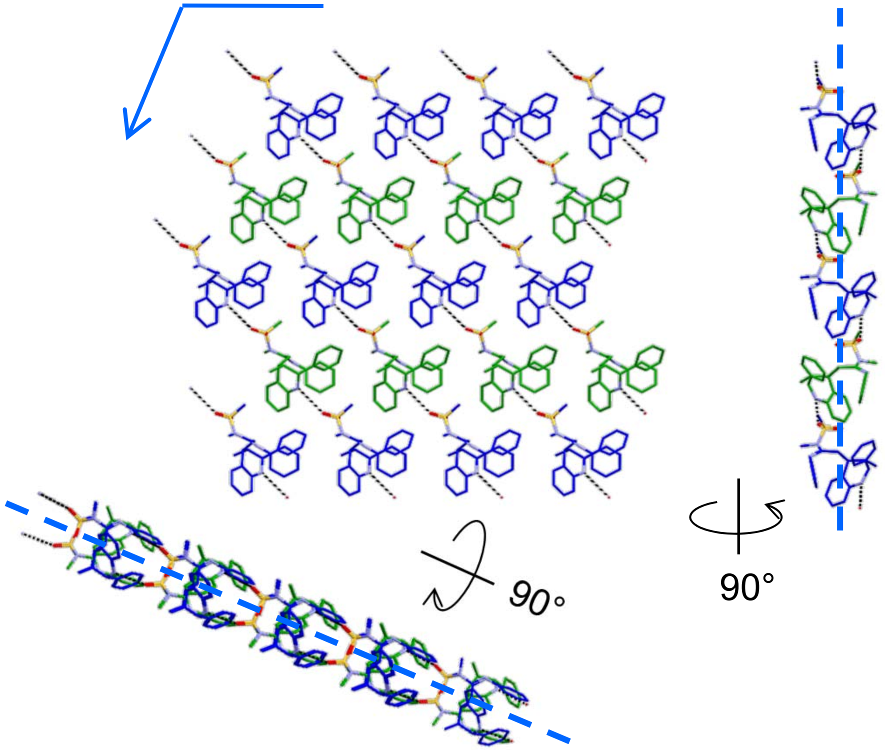
Projection along **a**

OLOKOR
(*P*1, *Z'*=2)



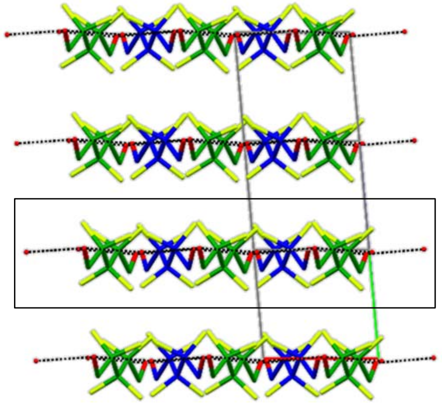
Layer $(01\bar{1})$





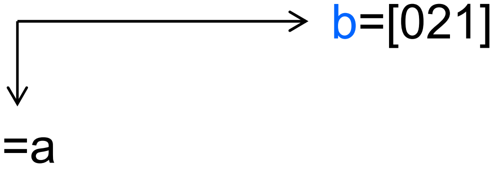
***p*11*a* (#5),**
***z'*=1**

Projection along [0$2\bar{1}$]

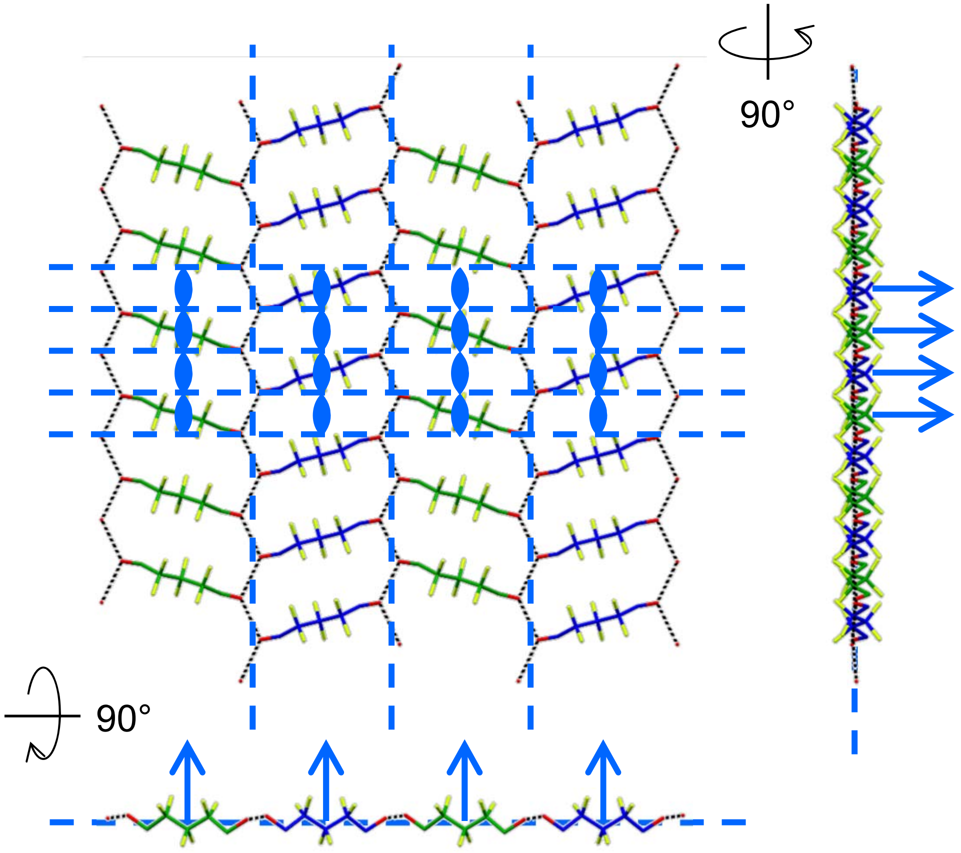


QUBPIN
(*P*1, *Z'*=2)

Layer (012)

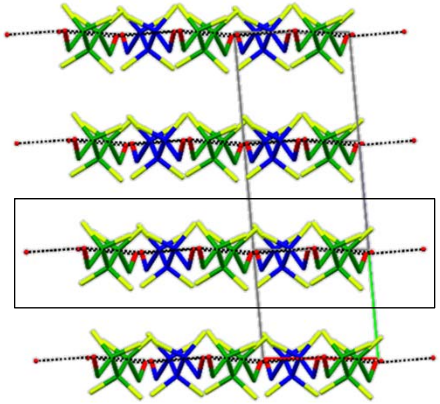


***pba2* (#25),**
***z'*=½**



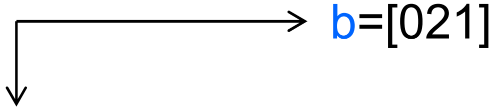
QUBPIN, con't (*P*1, *Z'*=2)

Projection along $[02\bar{1}]$



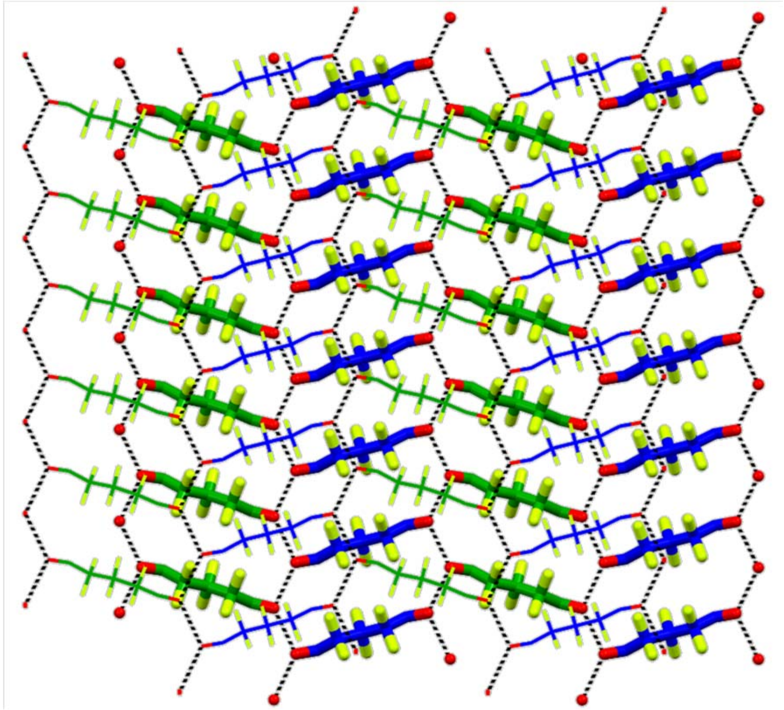
(012)

Two adjacent layers (012)



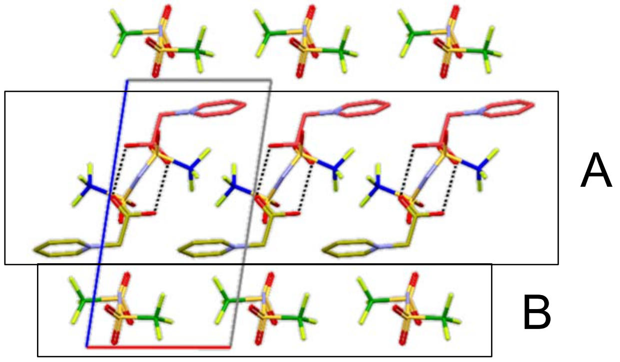
***pba*2 (#25), *z'*=½**

The molecules drawn with thinner lines are behind the molecules drawn with thicker lines



The fractional offsets between layers are -0.08 along a=a and 0.31 along b=$[02\bar{1}]$

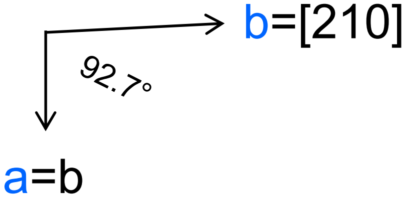
Projection along **b**



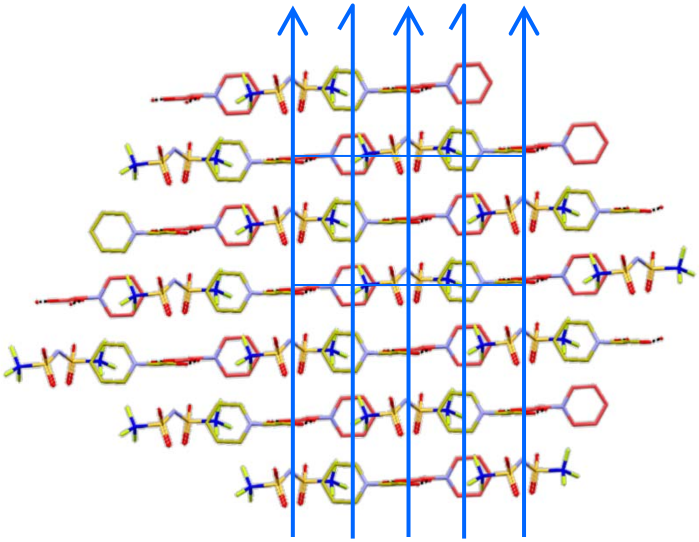
TOJRAM
($P1$, $Z'=2$)

1:1 salt of
N-(CH_2COOH)pyridinium and
$(F_3C)S(=O)_2NS(=O)_2(CF_3)^-$.
One anion is in layer A, the
other is in B

Layers (001) A and B

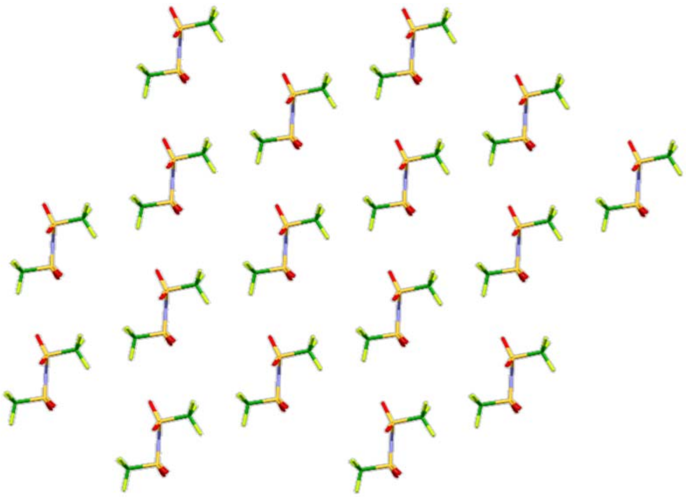


***c*211 (#10),**
***z'*=1 for**
the cation

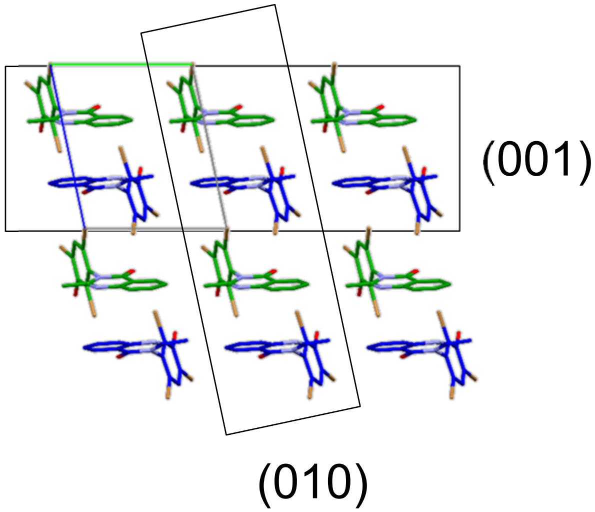


***p*1 (#1),**
***z'*=1 for**
one anion

(the layer group is not
*p*112 because the very
good twofold axis through
the anion is tilted away
from the layer by *ca* 20°)



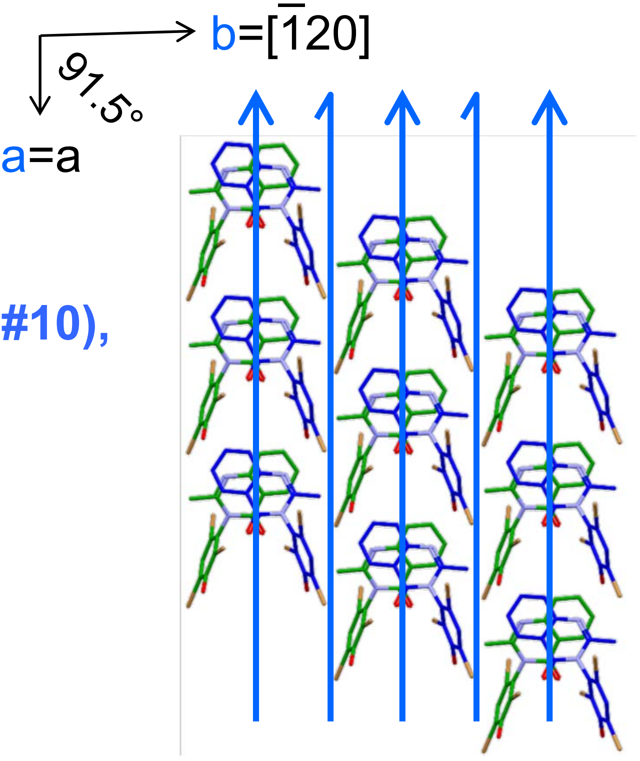
Projection along **a**



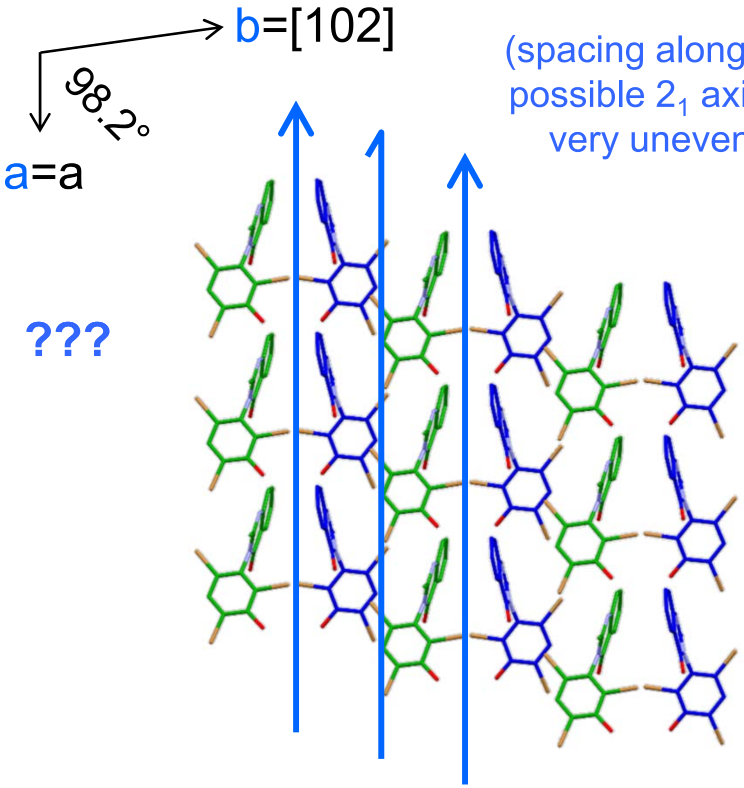
TUXLIJ
($P1$, $Z'=2$)

Layers (010) are better separated but layers (001) have higher approximate symmetry

Layers (001) and (010)



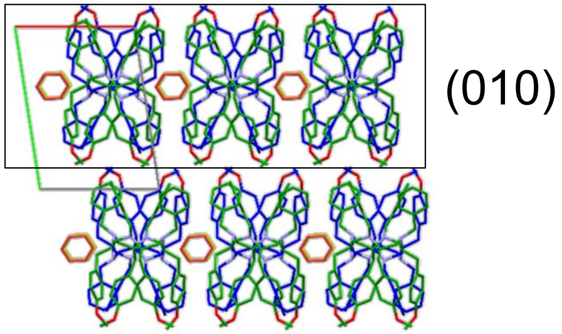
***c*211 (#10),**
***z'*=1**



???

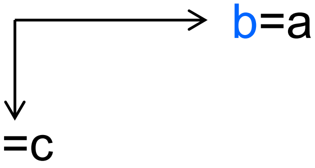
(spacing along the possible 2_1 axis is very uneven)

Projection along **c**

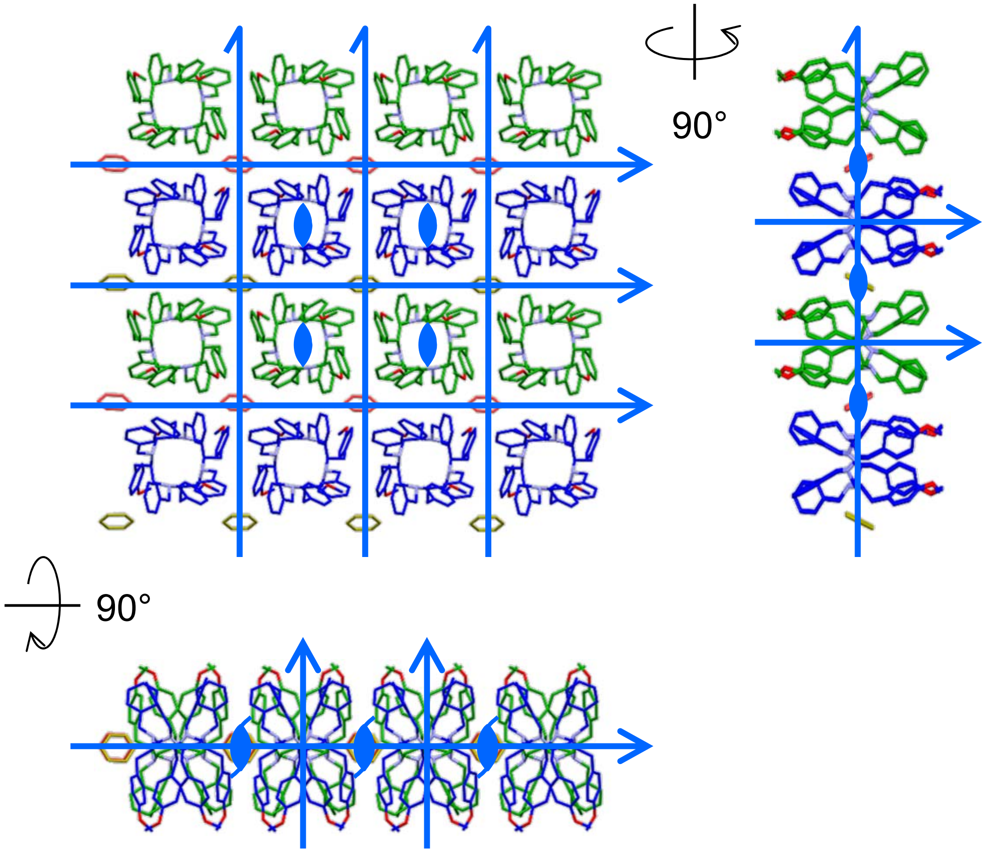


UJADOZ
(*P*1, *Z'*=2)

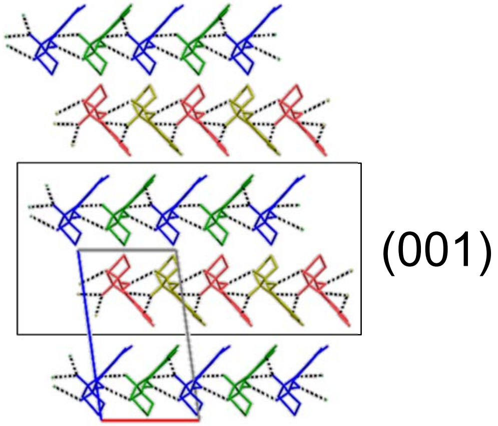
Layer (010)



***p*$2_1$22 (#20),**
***z'*=1/2**

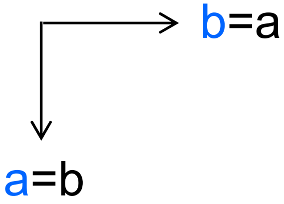


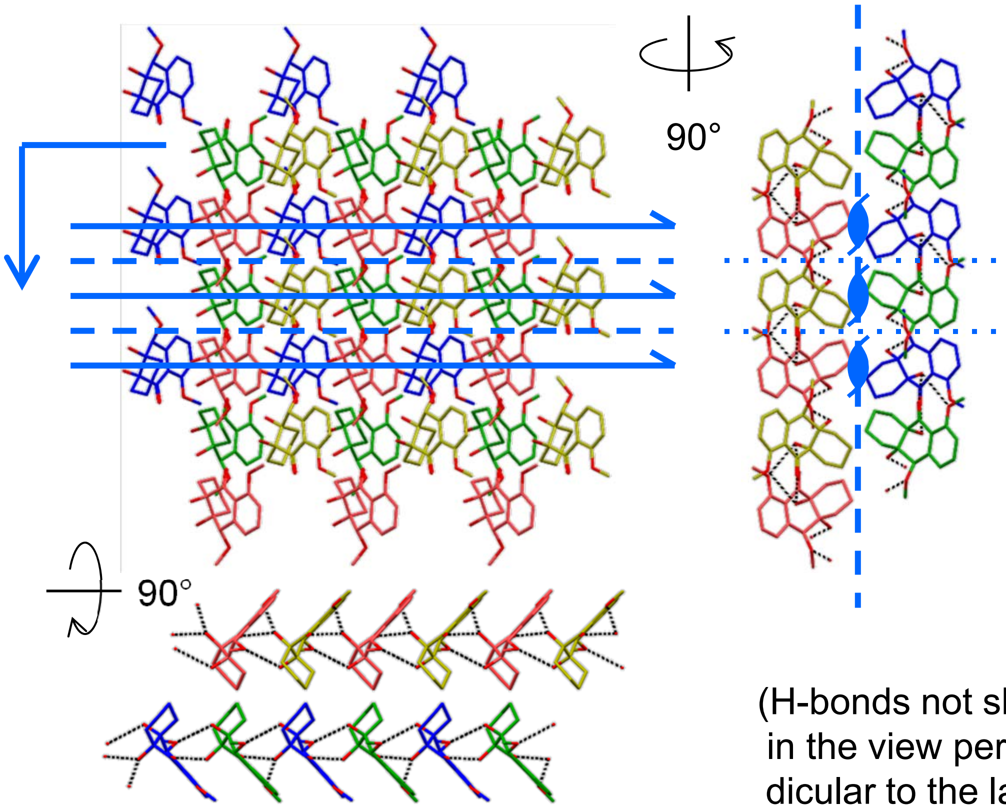
Projection along **b**



VEHDEU
($P1$, $Z'=4$)

Layer (001)

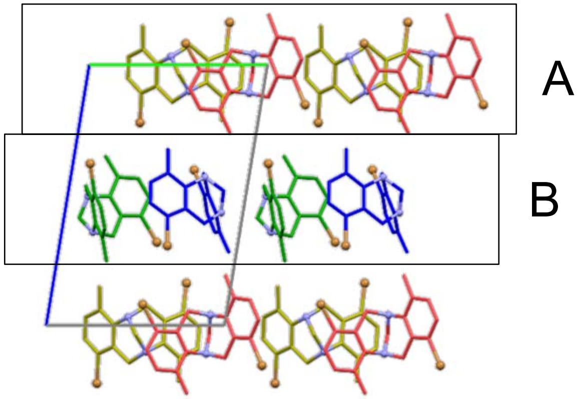




$pb2_1a$ (#33),
$z'=1$

(H-bonds not shown
in the view perpen-
dicular to the layer)

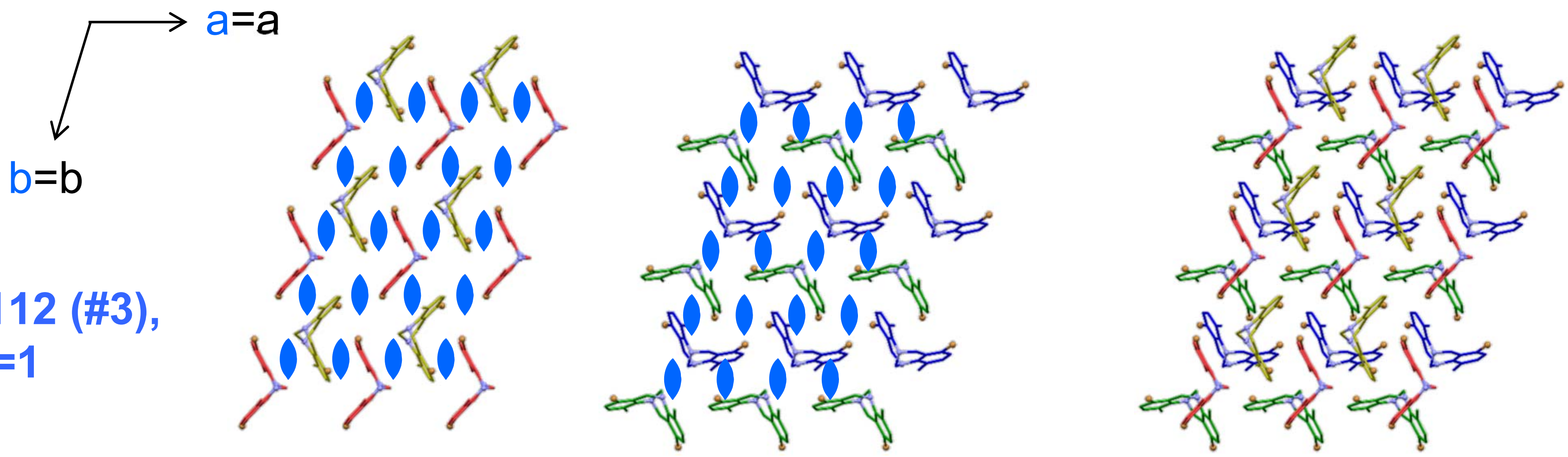
Projection along **a**



WAZSAT
($P1$, Z'=4)

(the twofold symmetric molecules are homochiral)

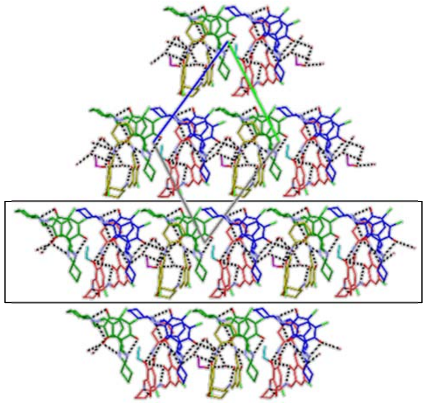
Layers (001) A, B, and a projection along **c*** of a pair of layers



p112 (#3),
***z'*=1**

The two layers have the same approximate symmetry but not the same packing; they cannot be superimposed even if rotation is allowed

Projection along **a**



XEVCEJ
($P1$, $Z'=4$)

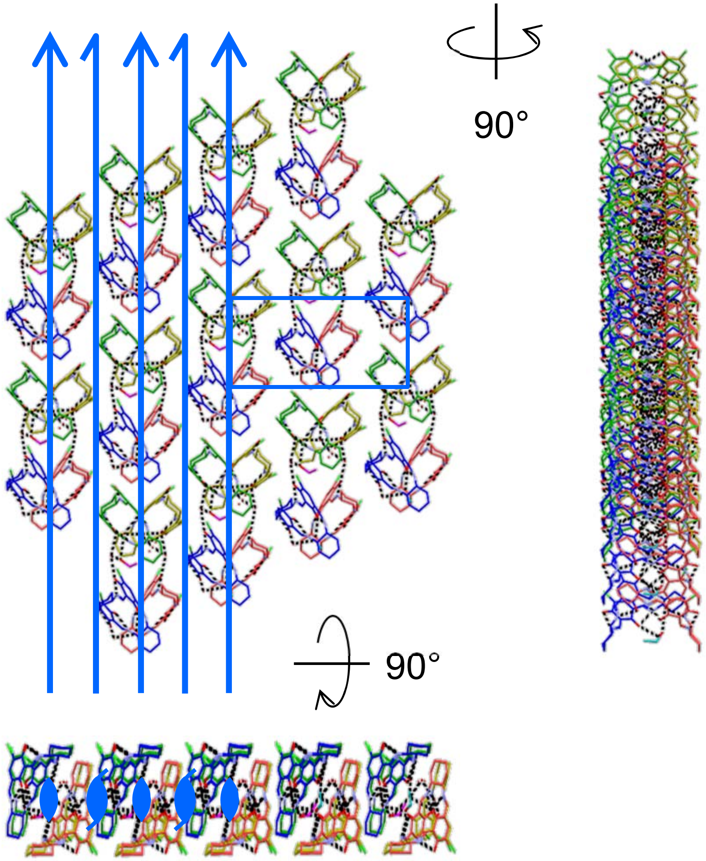
Layer (011)

b $=[31\bar{1}]/2$

a$=[1\bar{1}1]/2$

***c*211 (#10),**
***z'*=1**

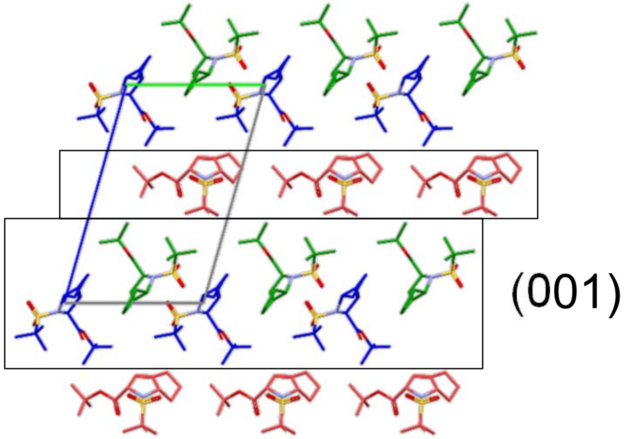
the approximate layer
cell is shown in blue



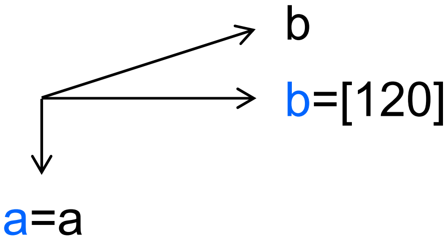
pseudo
translation
$[1\bar{1}1]/2$
$([3\bar{1}1]/2=$
$[1\bar{1}1]/2+[100])$

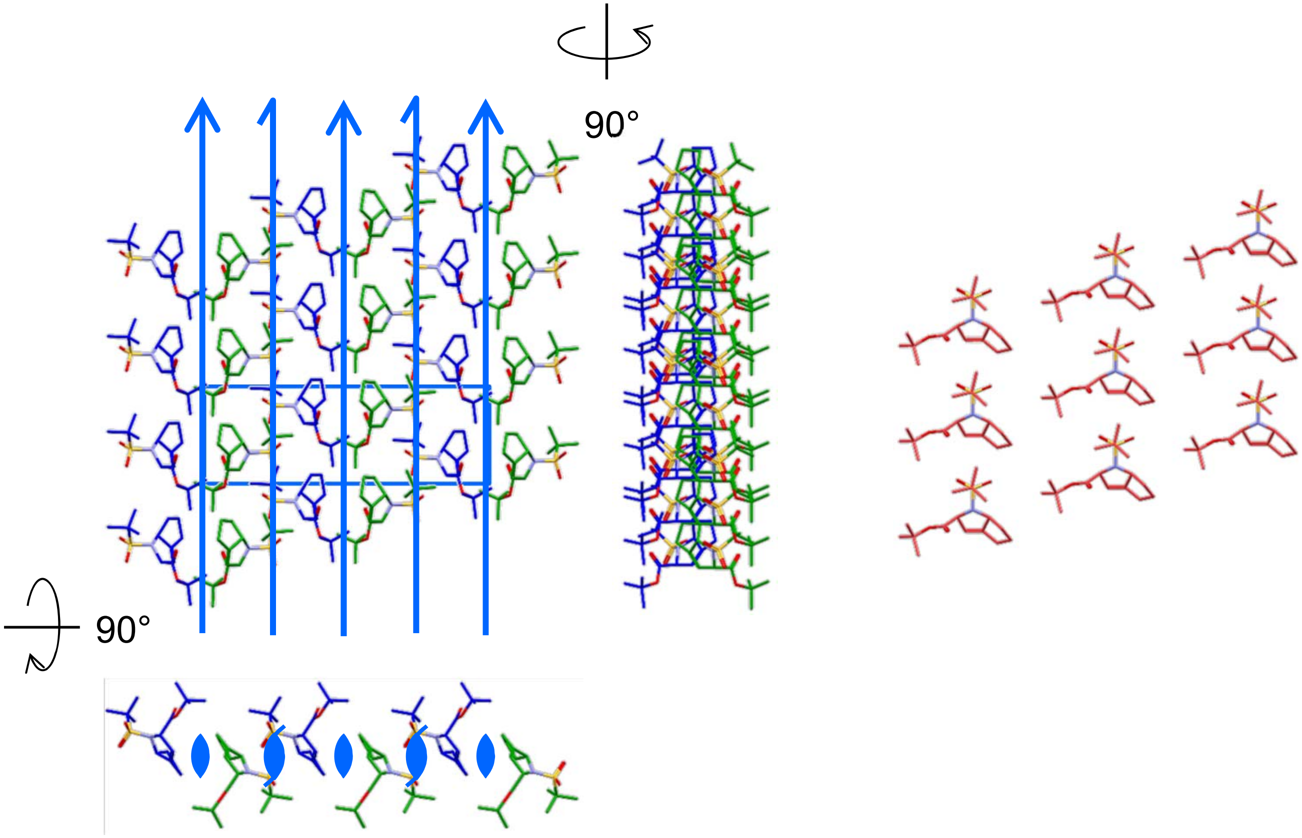
XURWEO
($P1$, Z'=3)

Projection along **a**



Layer (001)

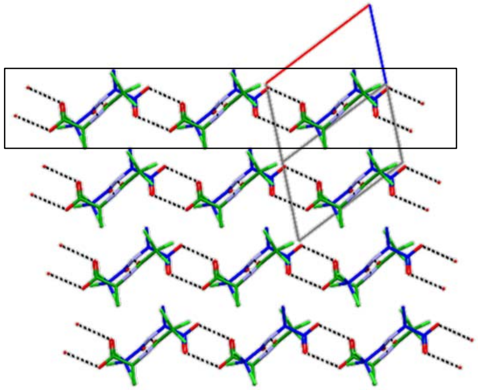




***c*211 (#10) and**
***c*1 (or, *p*1),**
both *z'*=1

the approximate layer cell is shown in blue

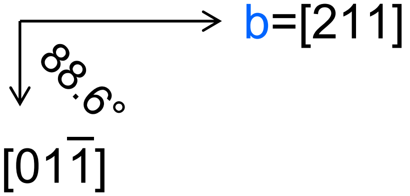
Projection along [01$\bar{1}$]



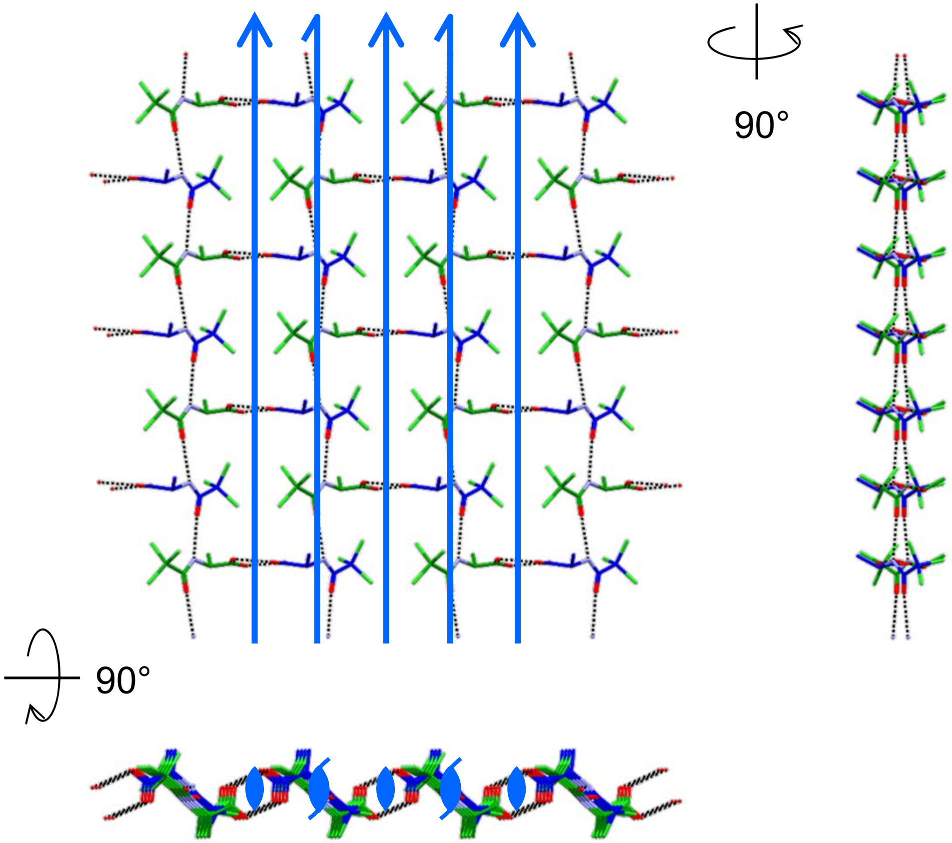
(111)

ZIYNAW
(*P*1, *Z'*=2)

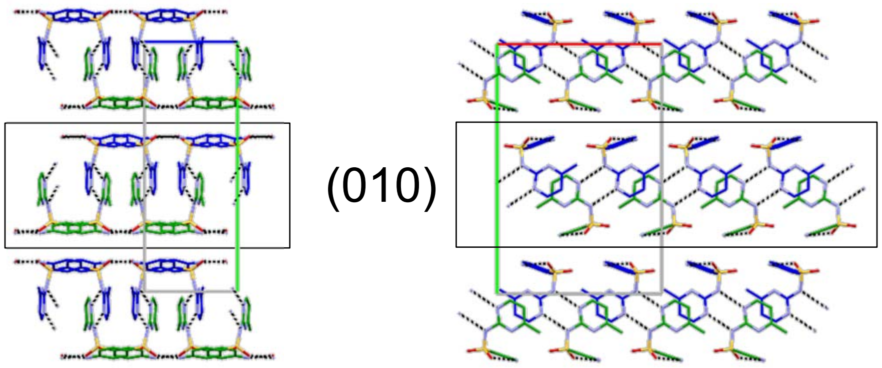
Layer (111)



c211 (#10),
***z'*=1**



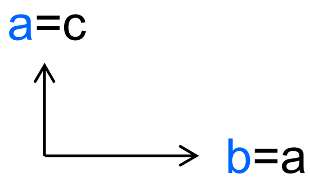
Projections along **a** and **c**



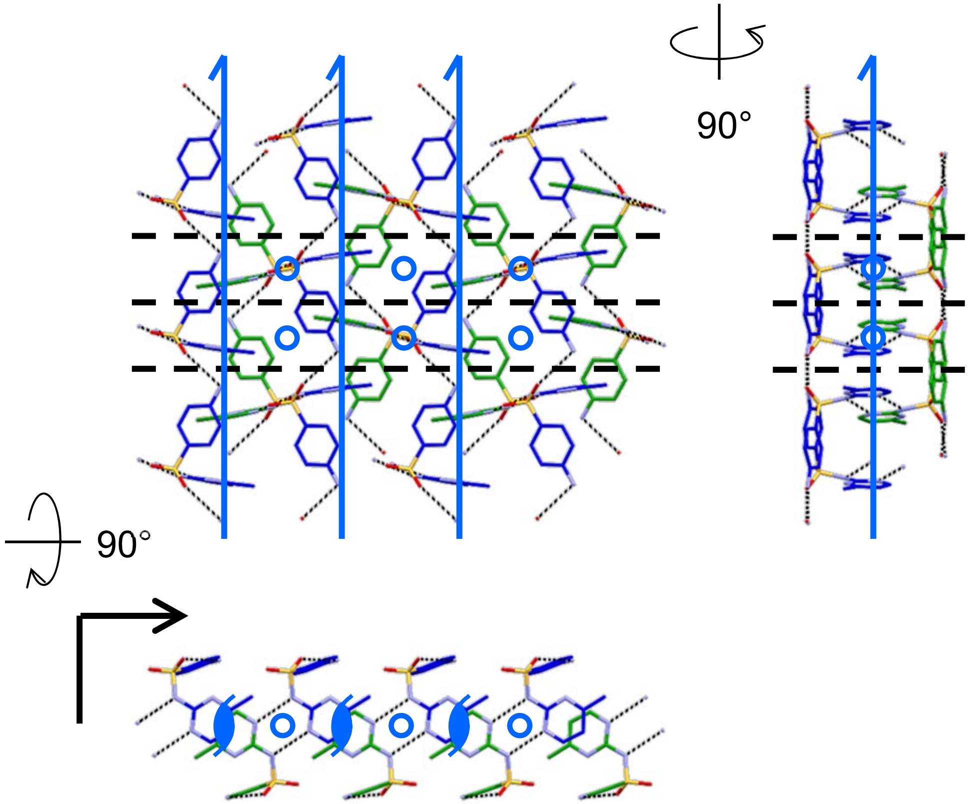
SLFNMA02 ($Pn2_1a$, $Z'=2$)

($Pn2_1a$ is $Pna2_1$ with the **b** and **c** axes switched)

Layer (010)



$p2_1/b11$ (#9), $z'=1$

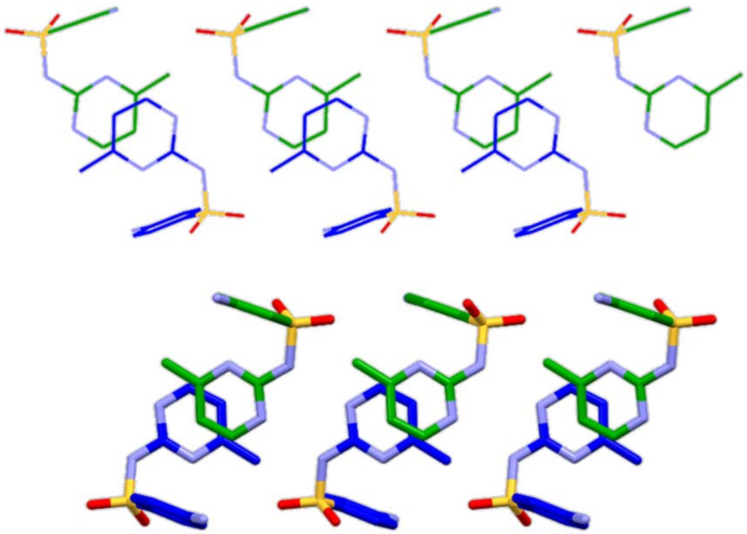


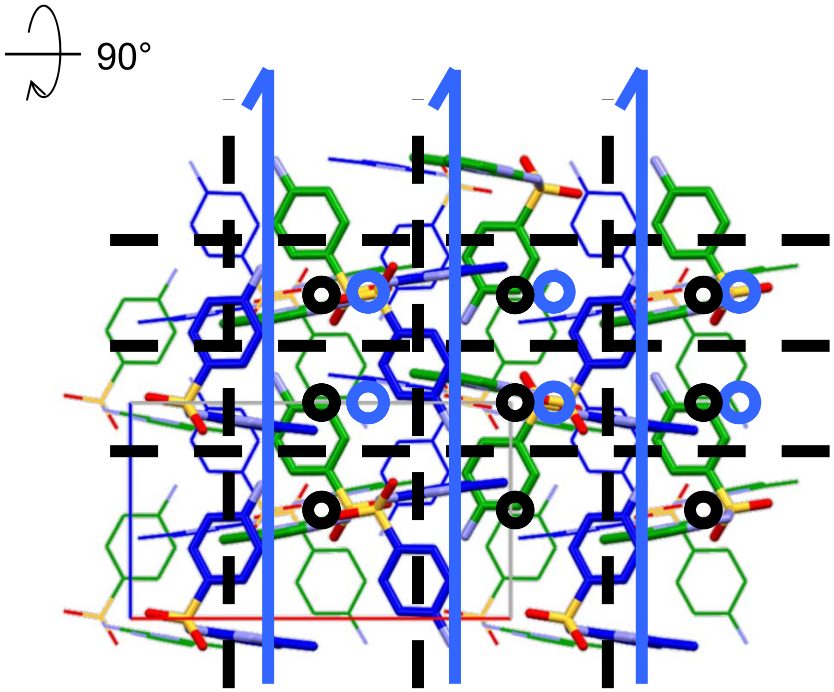
(See also next page)

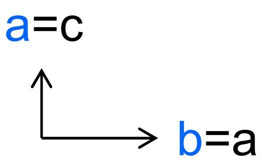
SLFNMA02, con't ($Pn2_1a$, $Z'=2$)

($Pn2_1a$ is $Pna2_1$ with the **b** and **c** axes switched)

Two layers (010)



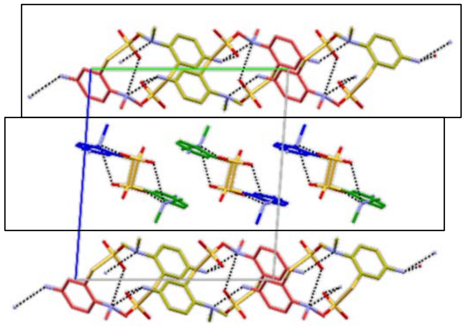




$p2_1/b11$ (#9), $z'=1$

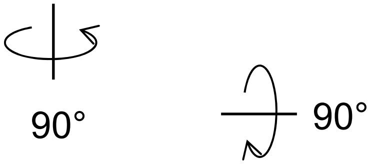
The symmetry elements shown in black apply to the whole structure; those shown in blue apply to the layer only. The offset between the two, mostly along **a**, means that the approximate layer symmetry cannot describe the 3-D structure.

Projection along

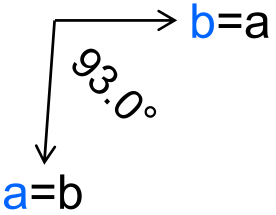


(001)

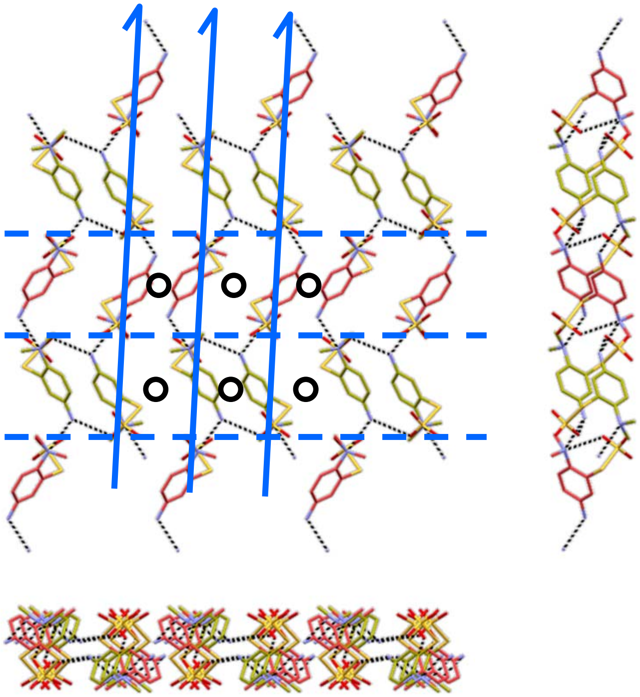
BOVDAS
($P\bar{1}$, $Z'=4$)



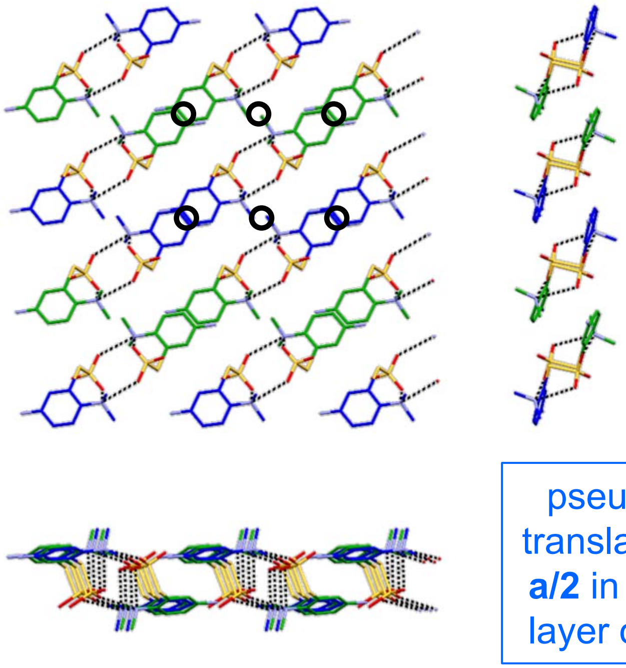
Layers (100) at $z=0$ and $z=½$



$p2_1/b11$ (#9), $z'=1$

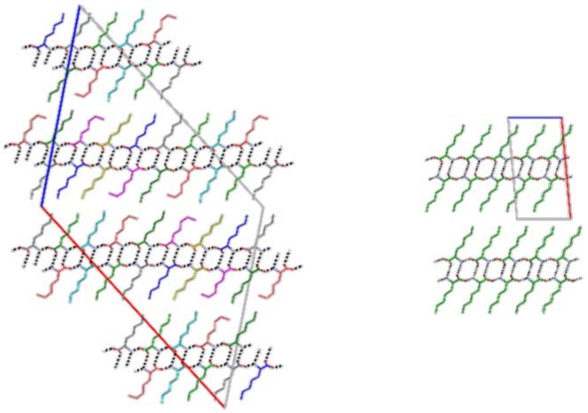


$p\bar{1}$, (#2), $z'=1$



pseudo translation **a/2** in this layer only

Projections along **b**



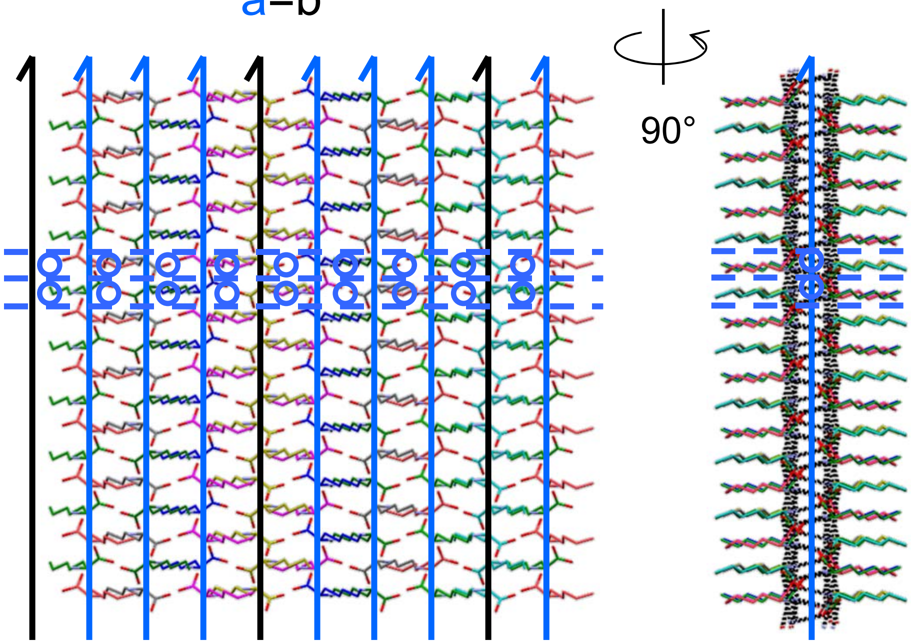
TETBUS02
($C2$, Z'=8 at 145 K);
TETBUS03
($P2_1/c$, Z'=1 At RT)

Layers

$(10\bar{1})$

b=$[10\bar{1}]/4$

a=b



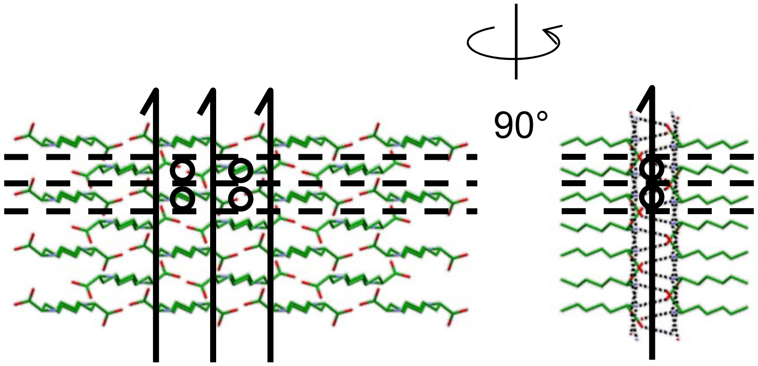
$p2_1/b11$ (#17),
z'=1

pseudo
translation
[101]/4

(100)

b=c

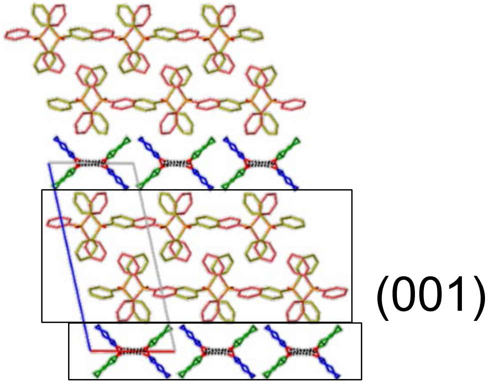
a=b



$p2_1/b11$ (#17),
z'=1

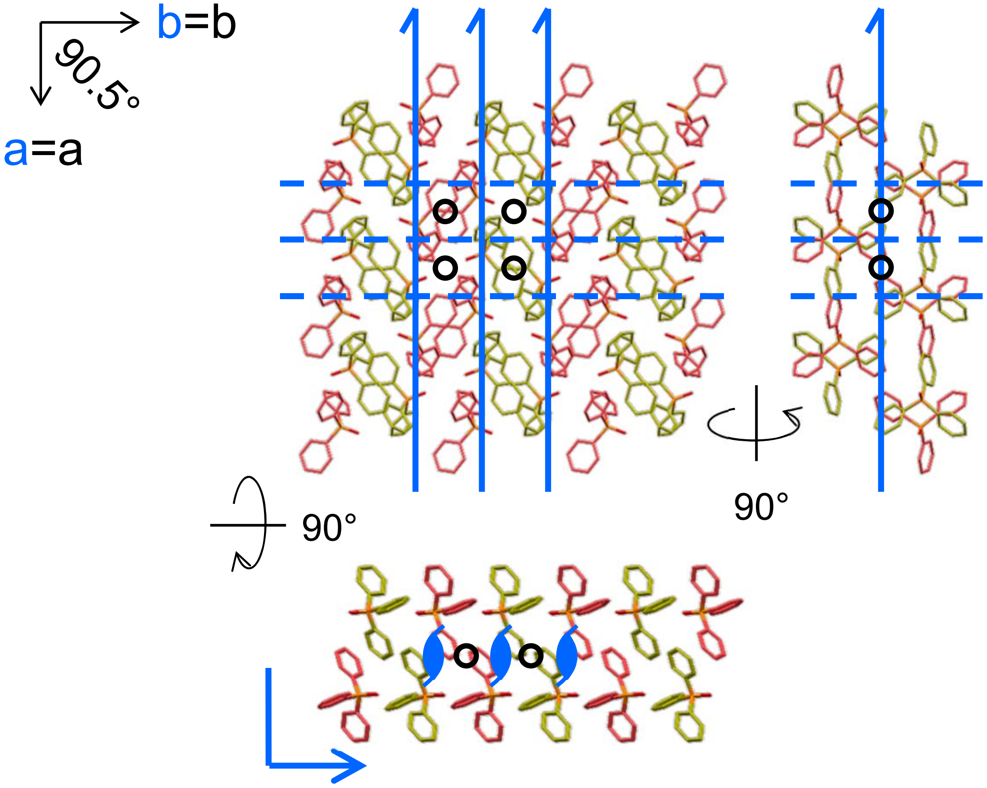
Projection along **b**

YIQGIP06
($P\bar{1}$, Z'=2)



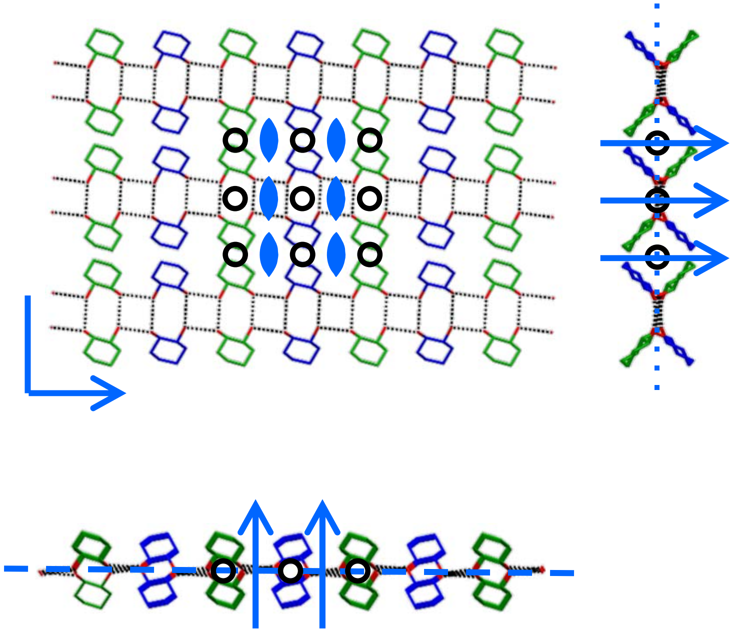
Layer (001)

$p2_1/b11$ (#17), z'=1



$p112/b$ (#7), z'=1

(std setting is $p112/a$)



(See also next page)

Layer of 1,2-cyclohexanediol molecules

YIQGIP0*n*
near 295 K

as refined in $P\bar{1}$, $Z'=2$
($n=6, 7, 8$)
disorder (less than 75:25) not shown;
individual layers are probably ordered

$p112/b$ (#7), $z'=1$
(std setting is $p112/a$)

as refined in $C2/c$, $Z'=1$
($n=9, 10, 11$)
near 50:50 disorder of R, S molecules

$p2/b11$ (#16), $z'=1$
$pbmb$ (#38), $z'=½$
(std setting is $pmaa$)

pbmb is a supergroup of both *p*112/*b* and *p*2/*b*11