STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 78 (2022)

Supporting information for article:

Pervasive approximate periodic symmetry in organic *P*1 structures

Carolyn Pratt Brock

Conventions

Residues (*i.e.*, crystallographically independent molecules and/or ions) are colored as in the CCDC program *Mercury* (lime green, bright blue, red, yellow, magenta, cyan, white, dark green, navy, brown for #1, #2, #3, …, #10) except that the shades have been darkened to make the light colors more visible.

In most cases the display style is capped sticks. Stereocenters are sometimes shown as spheres. If more than one layer is shown in a single image the first layer is shown as capped sticks, the second as wireframe, and the third as balls and sticks.

Anything shown in medium blue describes the approximate symmetry.

Axes are not usually labeled but they can be identified by color (red, green, blue for **a**, **b**, **c**).

Planes are labeled (*hkl*); directions are labeled [*xyz*]. Planes are labeled with their simplest Miller indices; no distinction is made between, *e.g.*, (110) and (220); only the orientation of the plane is specified. Similarly, directions are labeled with the simplest set of integers.

The primary rotation axis is vertical unless the approximate layer symmetry is *p*112 or unless a different direction is specified. If the only approximate symmetry is a glide the mirror normal is vertical unless the approximate layer symmetry is *p*11*a* or unless a different direction is specified.

A layer is always shown in projection along its normal unless a rotation is specified.

The symbols shown for twofold rotations usually, but may not always, indicate the sense of the rotation (*ie*, whether it is clockwise or counterclockwise).

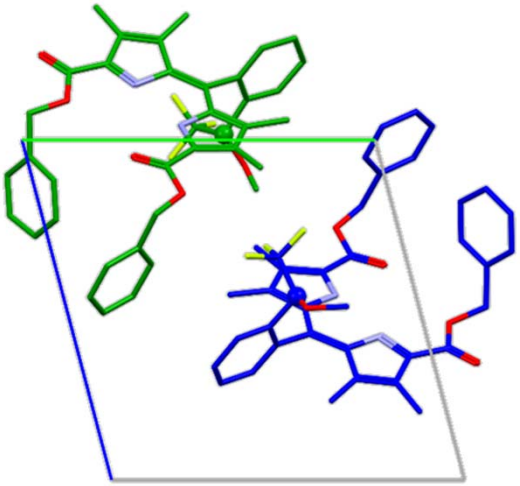
In most cases disorder, if there is any, is not shown. In almost no structure does reported disorder affect the identification of approximate symmetry. if it does the effect is explained.

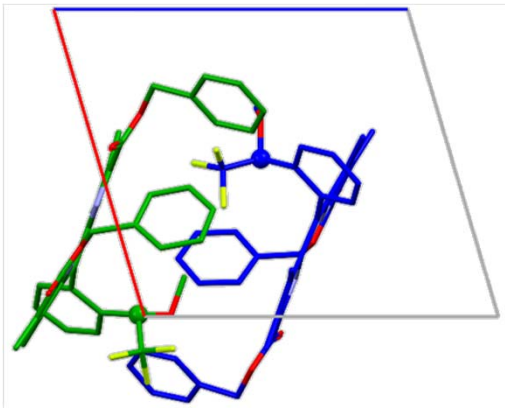
Structures that have approximate inversion symmetry
(by both distortion and mimicry)

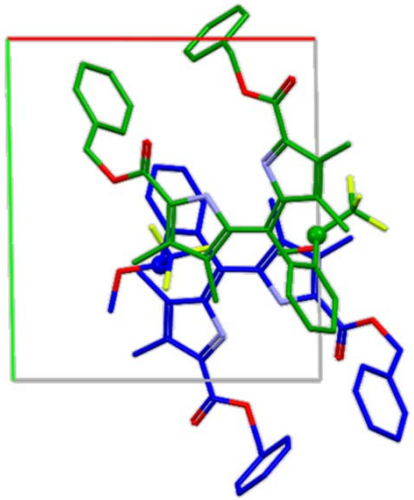
$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

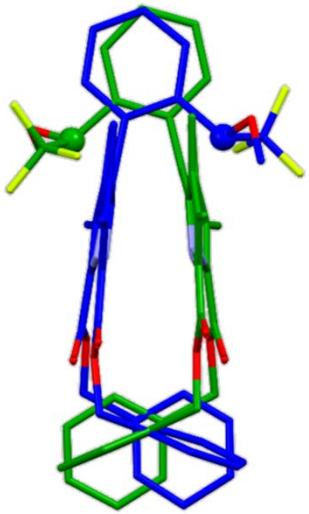
ASOGOE
(*P*1, *Z*=2)



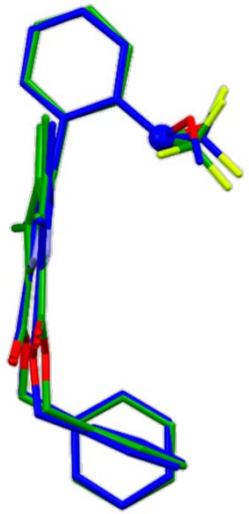




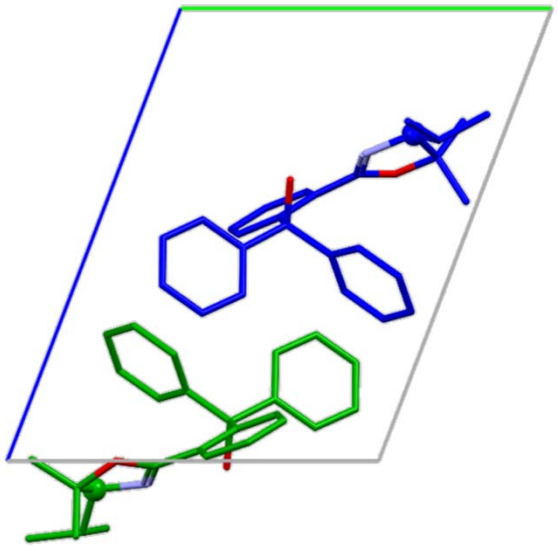
If the OMe and CF_3 substituents at the one stereocenter were switched in half of the molecules they would be enantiomers



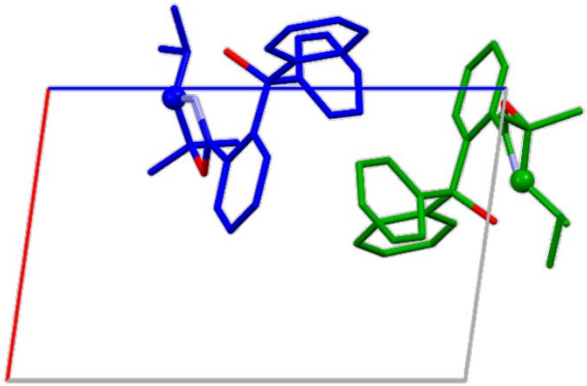
Best overlay of the two molecules as found and with one inverted



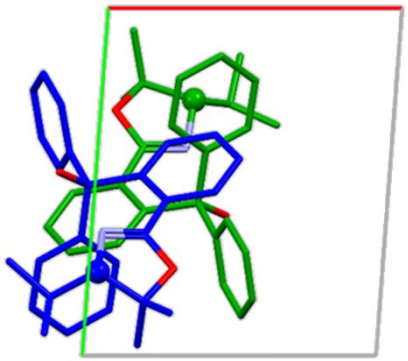
$P\bar{1}$ mimic



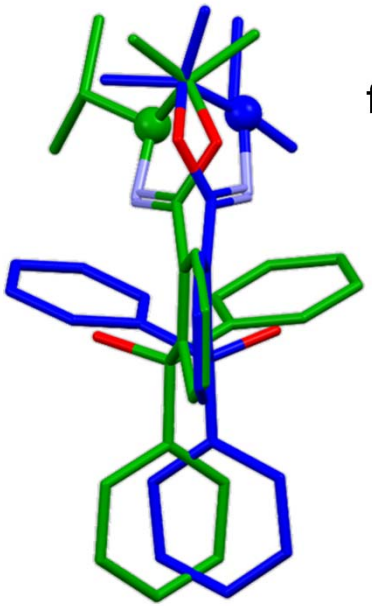
Views along **a**, **b**, and **c**



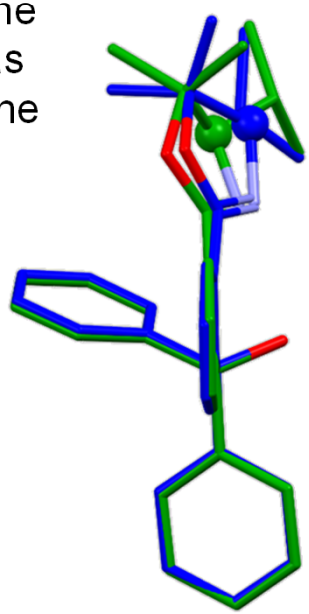
BENVIC
(*P*1, *Z*=2)



If the H and *i*-Pr substituents at the one stereocenter were switched in half of the molecules the two would be enantiomers



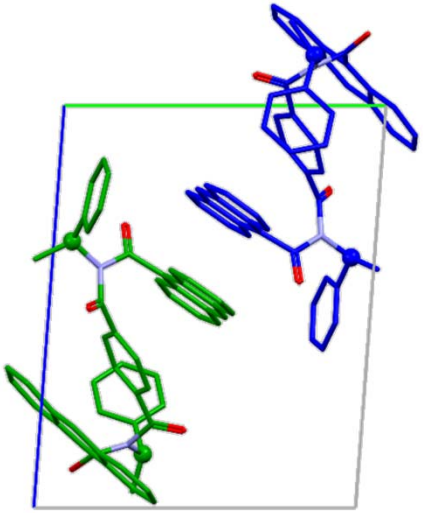
Best overlay of the two molecules as found and with one inverted

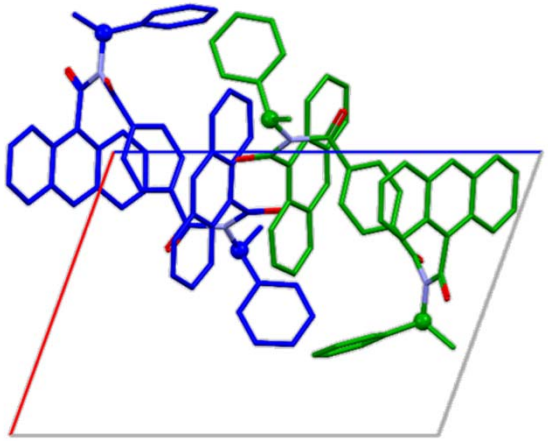


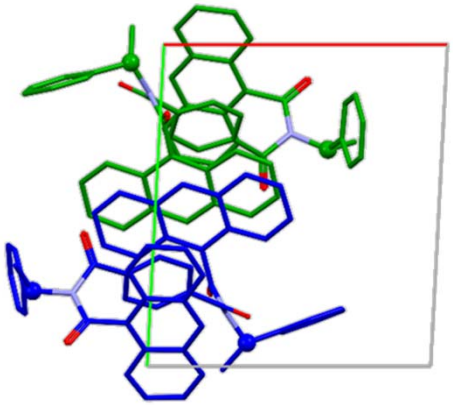
$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

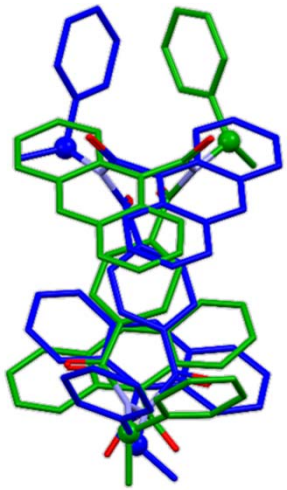
BIXHAS
(*P*1, *Z*=2)



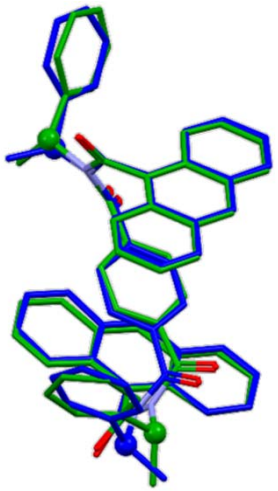




If the H and Me substituents at the two stereocenters were both switched in half of the molecules the two would be enantiomers



Best overlay of the two molecules as found and with one inverted

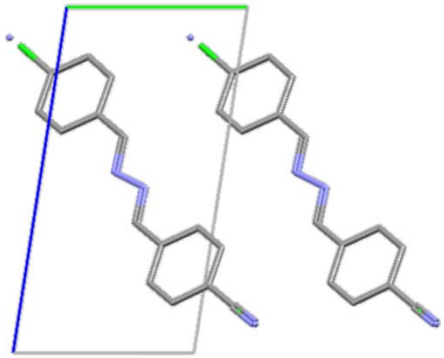


Distorted $P\bar{1}$ (achiral)

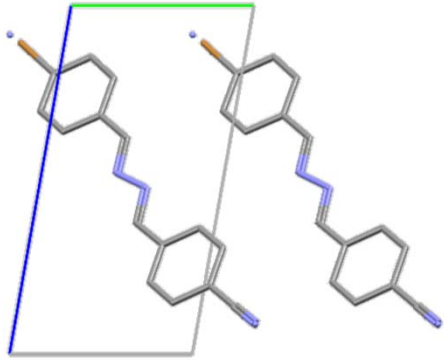
DIWGAS01,
DIWGEW,
DIWGIA
($P1$, Z=1)

4-cyano-4'-*X*-benzalazine

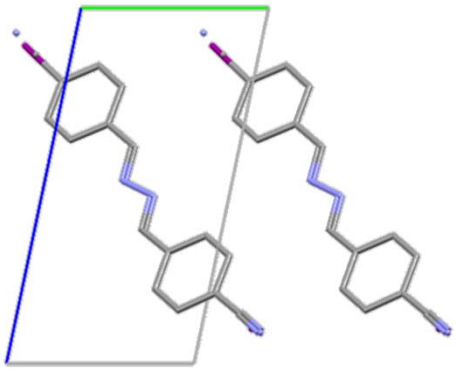
Views along **a**



4-Cl
disorder 67:33
at 174 K (R=0.045)



4-Br
disorder 81:19
at 174 K (R=0.025)



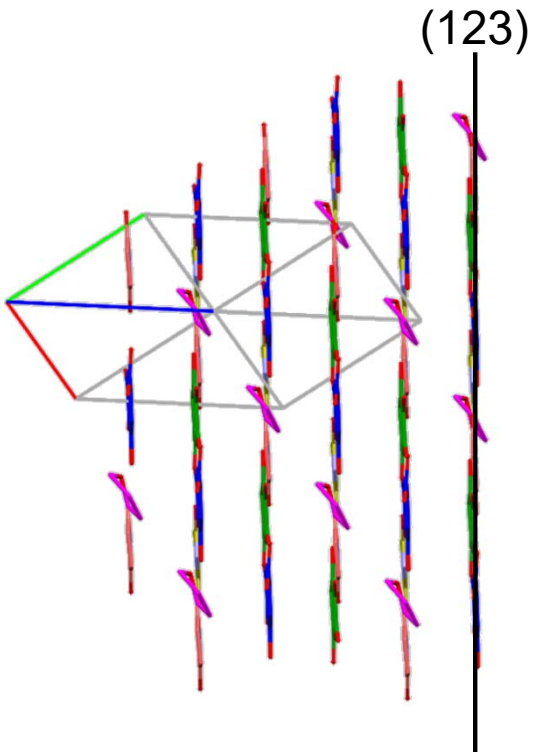
4-I
disorder 70:30
at 173 K (R=0.023)

If the disorder were 50:50 the space group would be $P\bar{1}$, but since the molecules seem very unlikely to reorient in the crystal the disorder must have been established during crystal growth

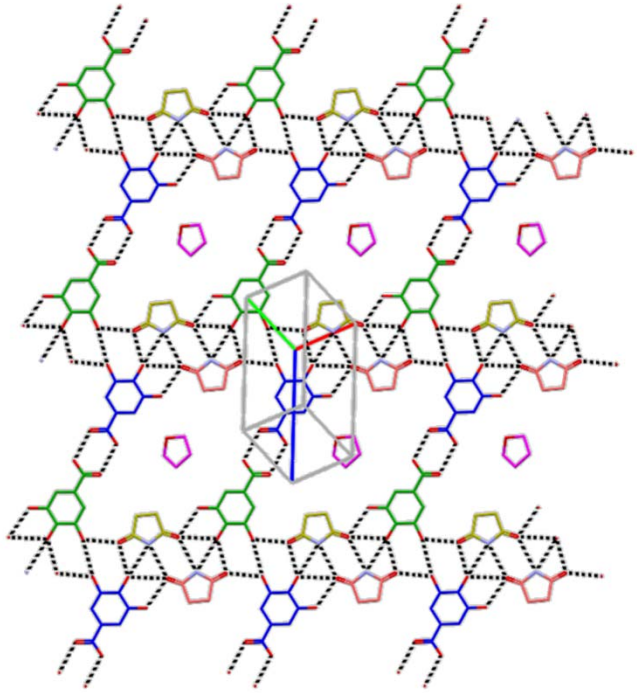
Distorted $P\bar{1}$ (achiral)

DUNDOH
(*P*1, *Z*=2)

View along [$11\bar{1}$]



A layer (123)

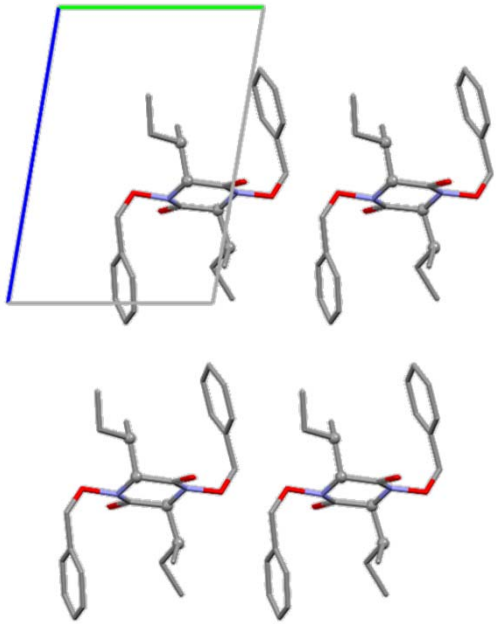


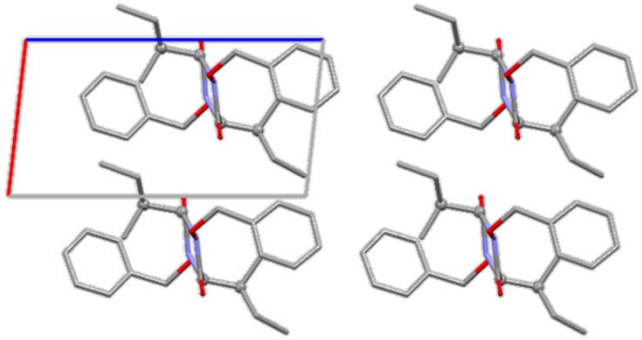
If the space group were $P\bar{1}$ the included THF molecule would be disordered around an inversion center. Structure was determined at 110 K where the THF was found to be ordered

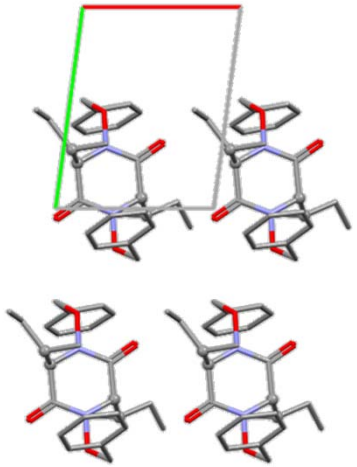
$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

EYOLAG
(*P*1, *Z*=1)





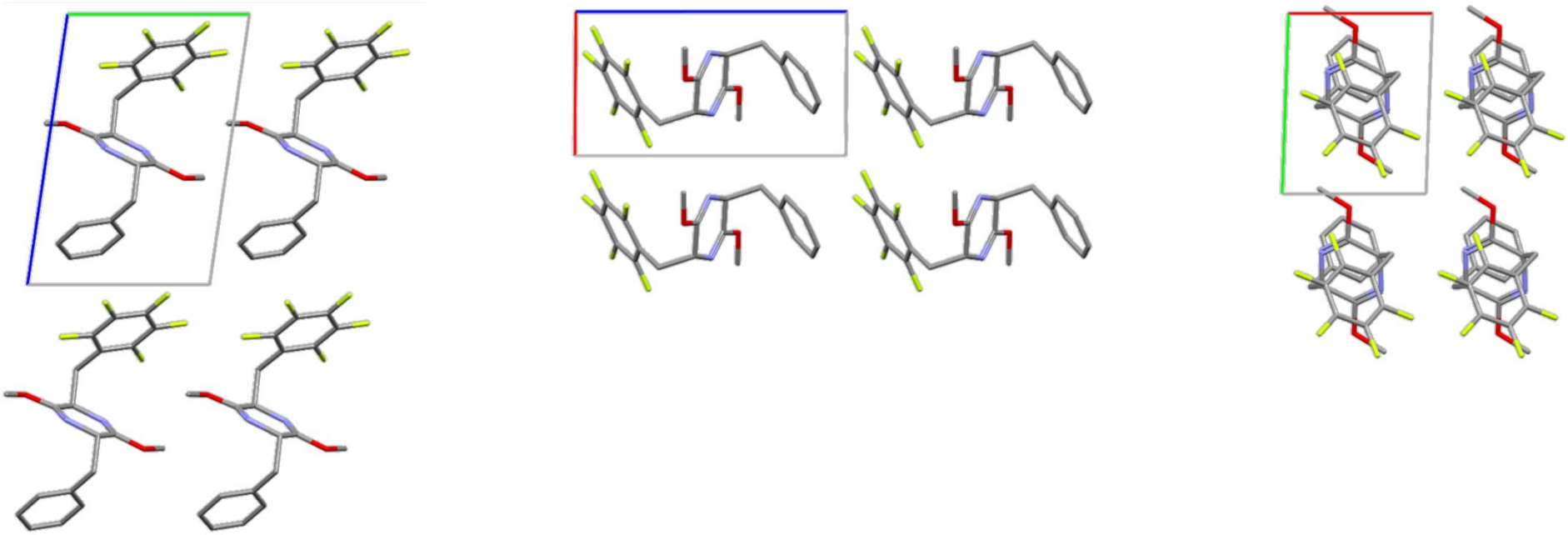


The two stereocenters in the C_4N_2 ring are heterochiral. The two CHMeEt substituents are homochiral. The molecule mimics inversion symmetry

$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

FIYPEI
(*P*1, *Z*=1)

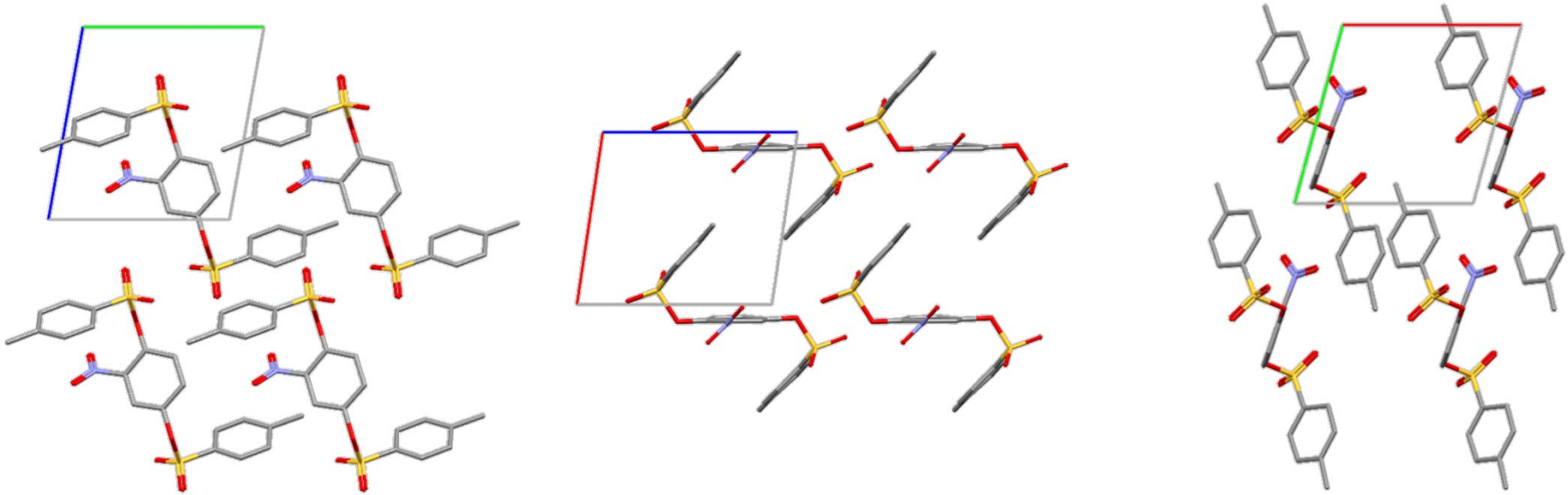


The molecule has approximate inversion symmetry except for the difference between the C_6H_5 and C_6F_5 substituents. The two ring types lie face-to-face as expected so that there is an approximate inversion center between them

$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

GOFTIF
(*P*1, *Z*=1)

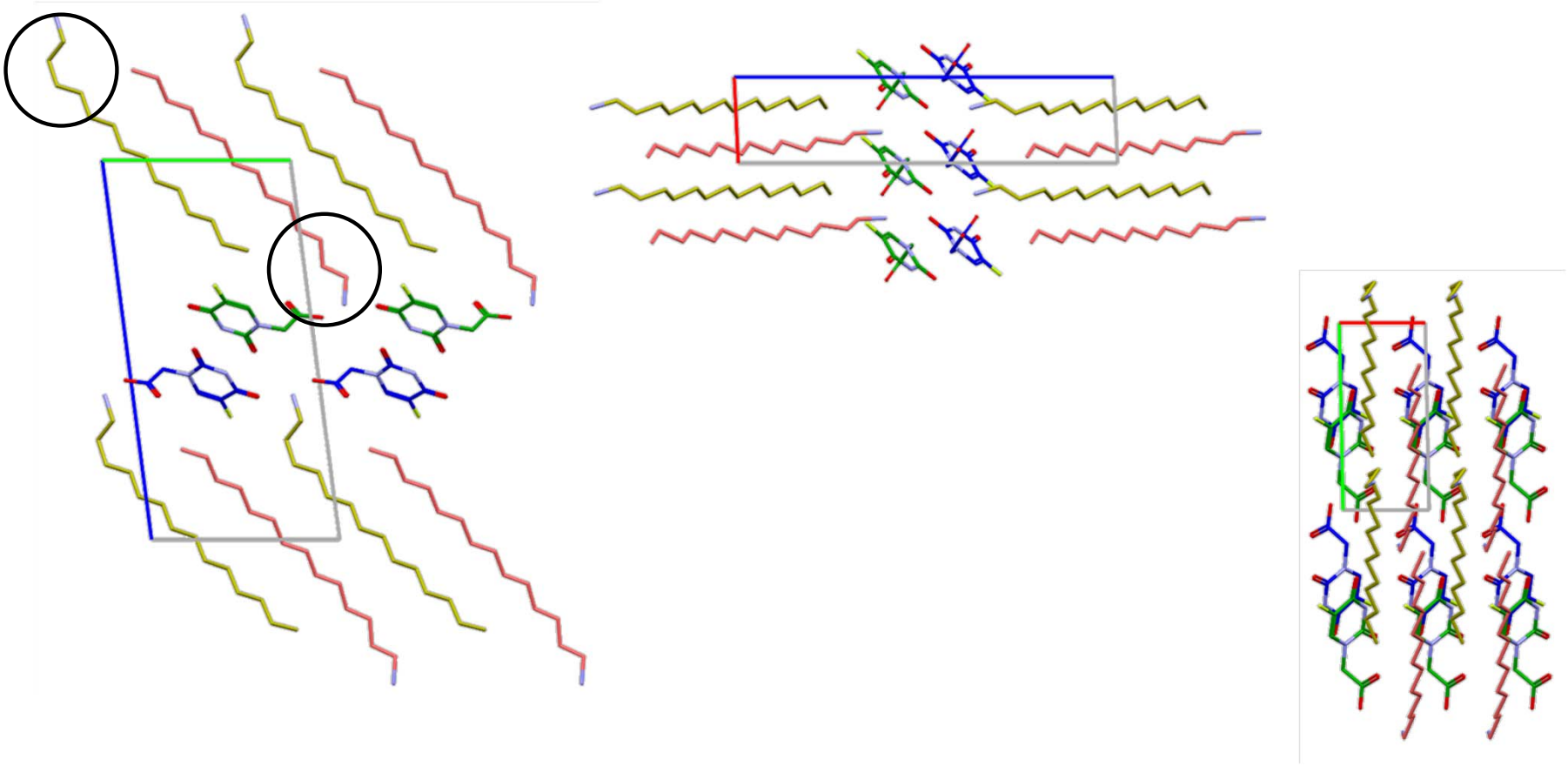


The nitro group breaks the inversion symmetry of the rest of the molecule but that substituent is quite near the molecular centroid and is shielded from intermolecular interactions. Overall the structure has good approximate symmetry $P\bar{1}$

Distorted $P\bar{1}$ (achiral)

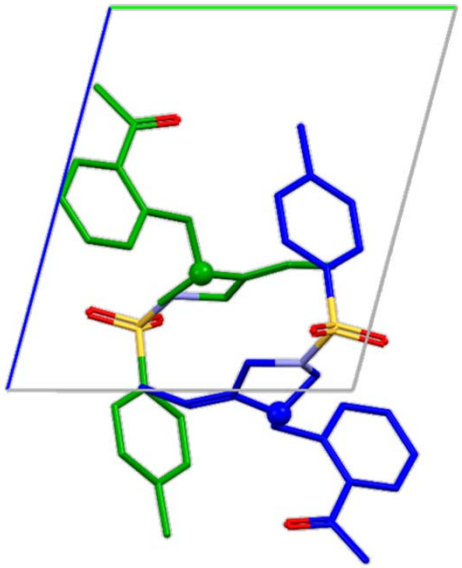
GOJLEZ
(*P*1, *Z*=2)

Views along **a**, **b**, and **c**

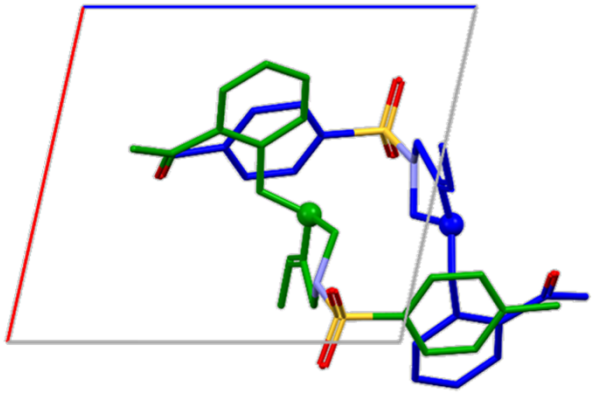


The deviations from $P\bar{1}$ symmetry are small but obvious.
Structure was determined at 115 K; it might be more symmetric at RT

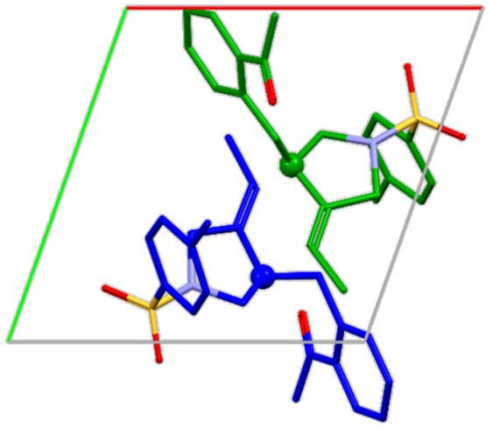
$P\bar{1}$ mimic



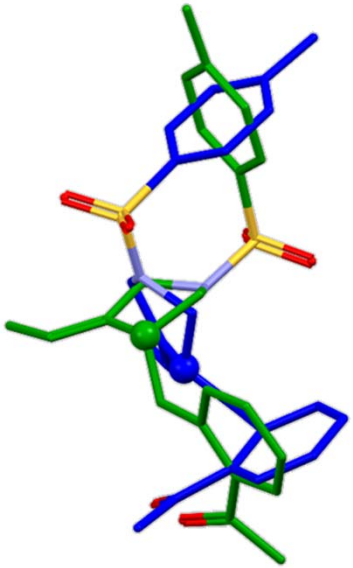
Views along **a**, **b**, and **c**



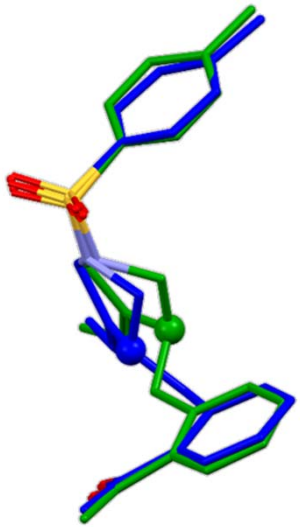
HIYDEZ
(*P*1, *Z*=2)



The conformations of the C_4N rings differ in the two homochiral molecules; they also differ by inversion at the N atom

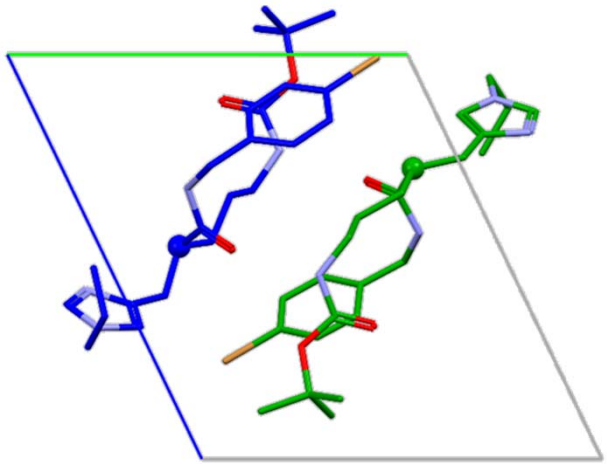


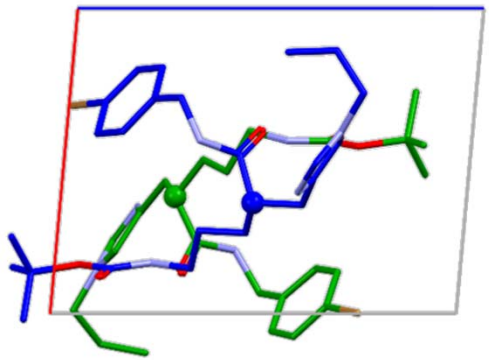
Best overlay of the two molecules as found and with one inverted



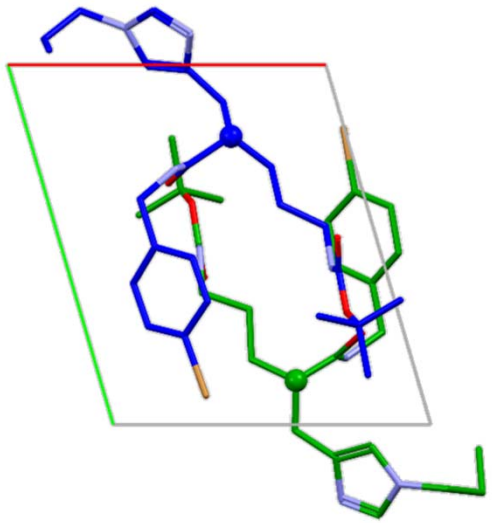
$P\bar{1}$ mimic

Views along **a**, **b**, and **c**



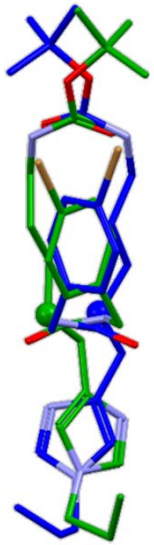


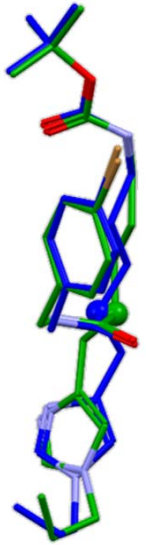
ICUGIY
(*P*1, *Z*=2)



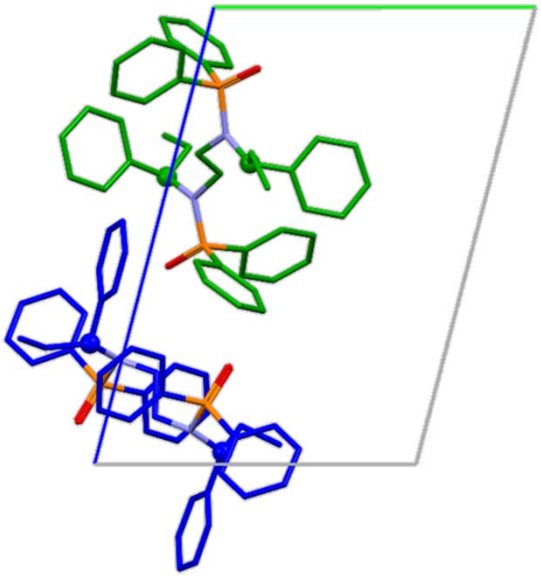
The one stereocenter is near the center of the quite flexible molecule
(the disorder in the *n*-Bu substituents is not shown)

Best overlay of the two molecules as found and with one inverted

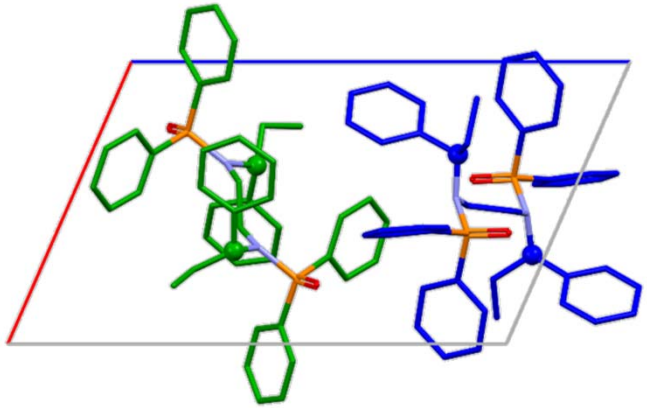




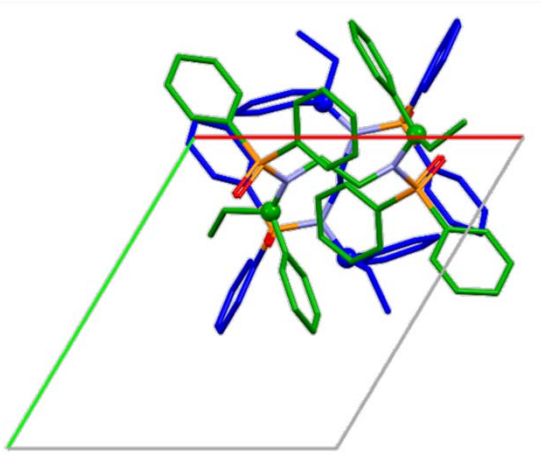
$P\bar{1}$ mimic



Views along **a**, **b**, and **c**

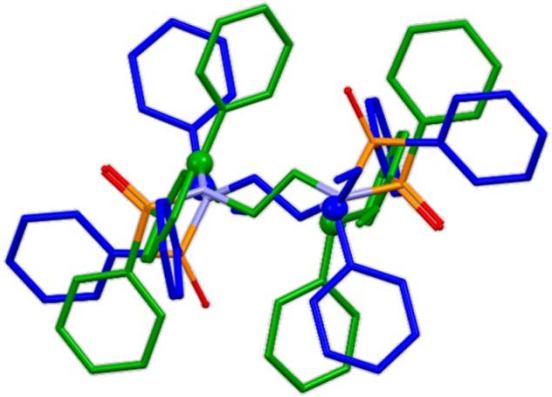


LESMEC
(*P*1, *Z*=2)



Mimic of a $P\bar{1}$ structure with *Z*=2, *Z'*=1=2(½).
If the H and Et substituents at one of the two stereo-centers in each molecule were switched then each molecule would have good inversion symmetry.
The two molecules have different conformations.

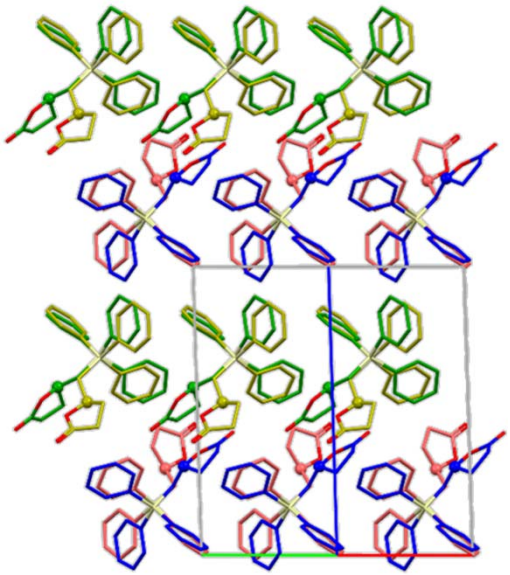
Best overlay of the two molecules as found showing that they have different conformations but that each has approximate inversion symmetry

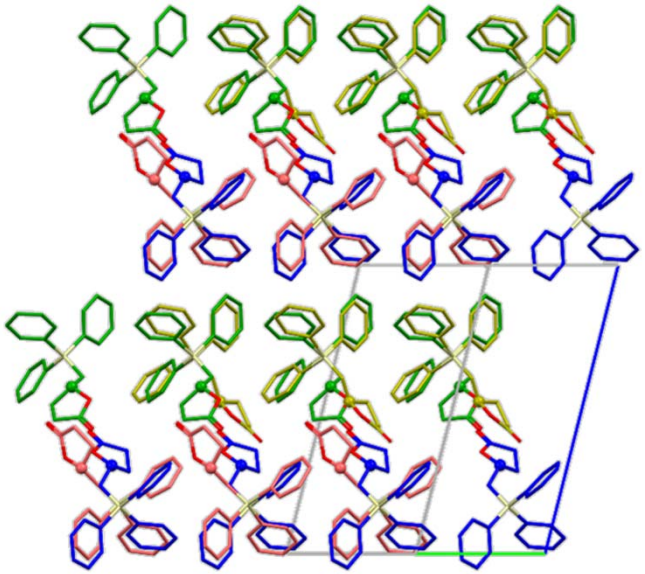


$\bar{1}$ mimic plus (includes approximate translation)

LEYXET
(*P*1, *Z*=4)

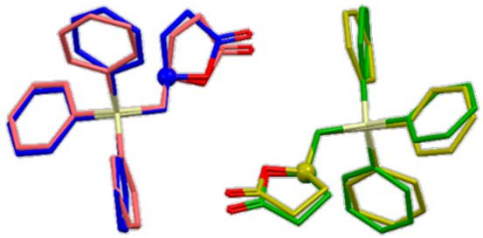
Views along [110] and [1$\bar{1}$0]

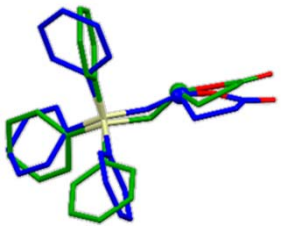


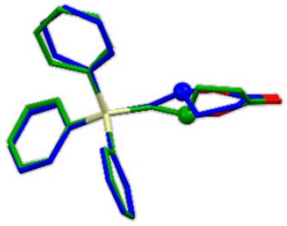


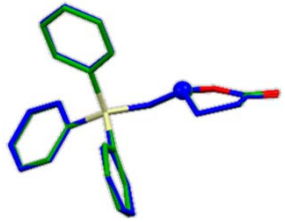
Approximate *P*$\bar{1}$,
Z=2, *Z'*=1
axes [110]/2, [1$\bar{1}$0],
[001]
(or [110], [1$\bar{1}$0]/2,
[001])

Best overlays of #1 and #2 as observed,
with inversion, and with flexibility





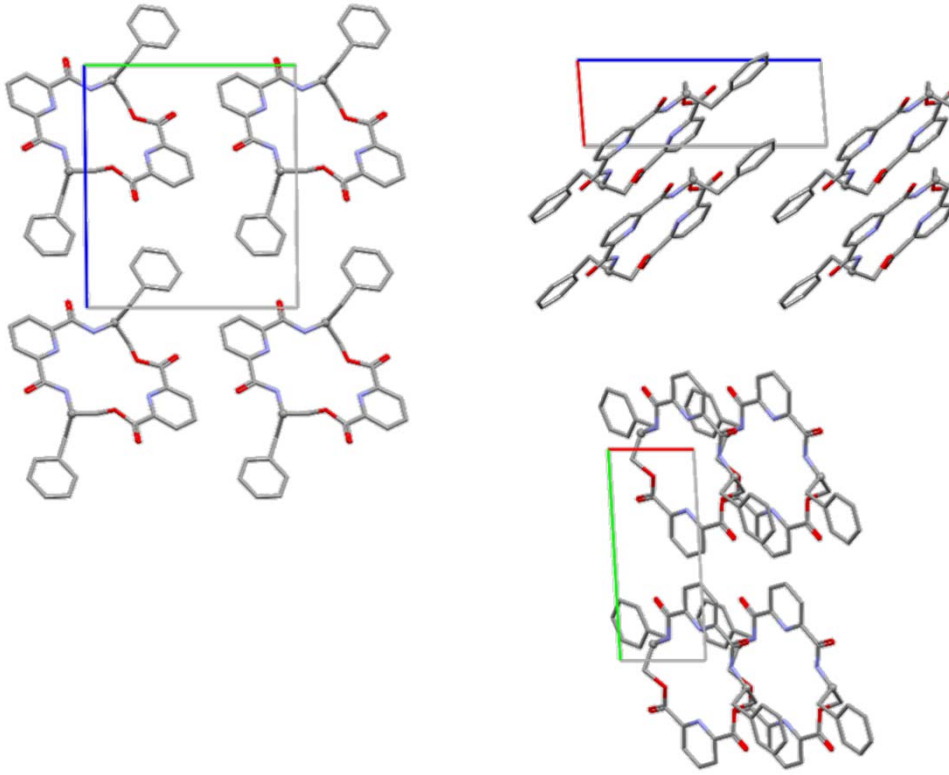




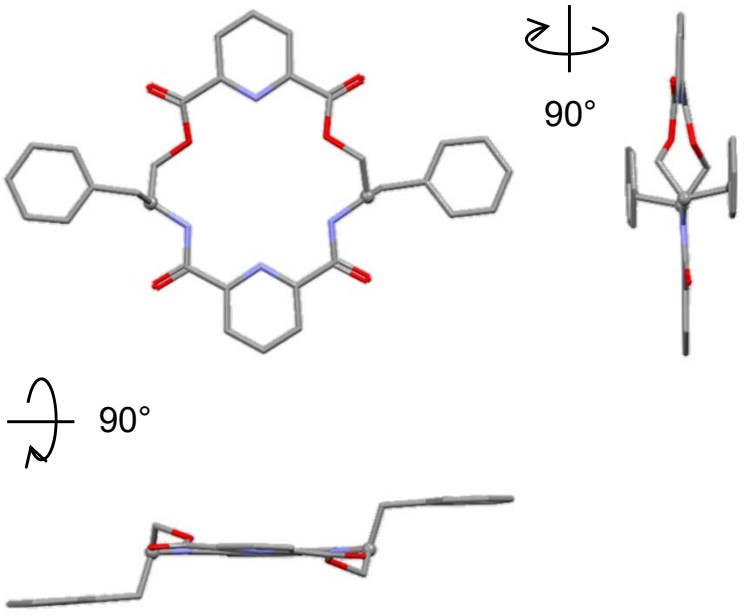
$P\bar{1}$ mimic

LIHLUL
(*P*1, *Z*=1)

Views along **a**, **b**, and **c**



Views of the molecule



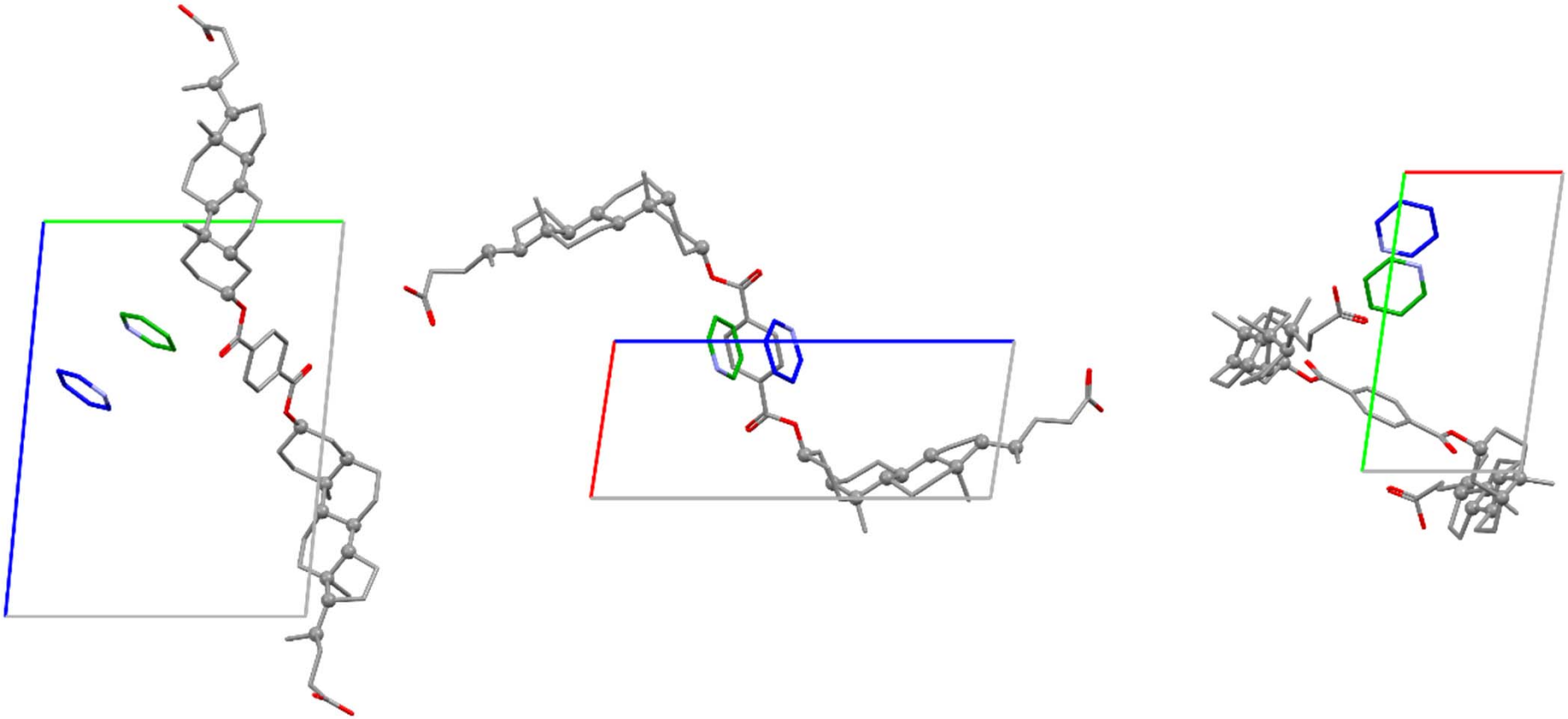
Inversion symmetry would require that the ring –O- atoms be the same as the two ring –NH- groups. The position and orientation of the CH_2Ph substituents contributes to the approximate symmetry.

$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

MIZQAO01
(*P*1, *Z*=1)

1:2 pyridine solvate

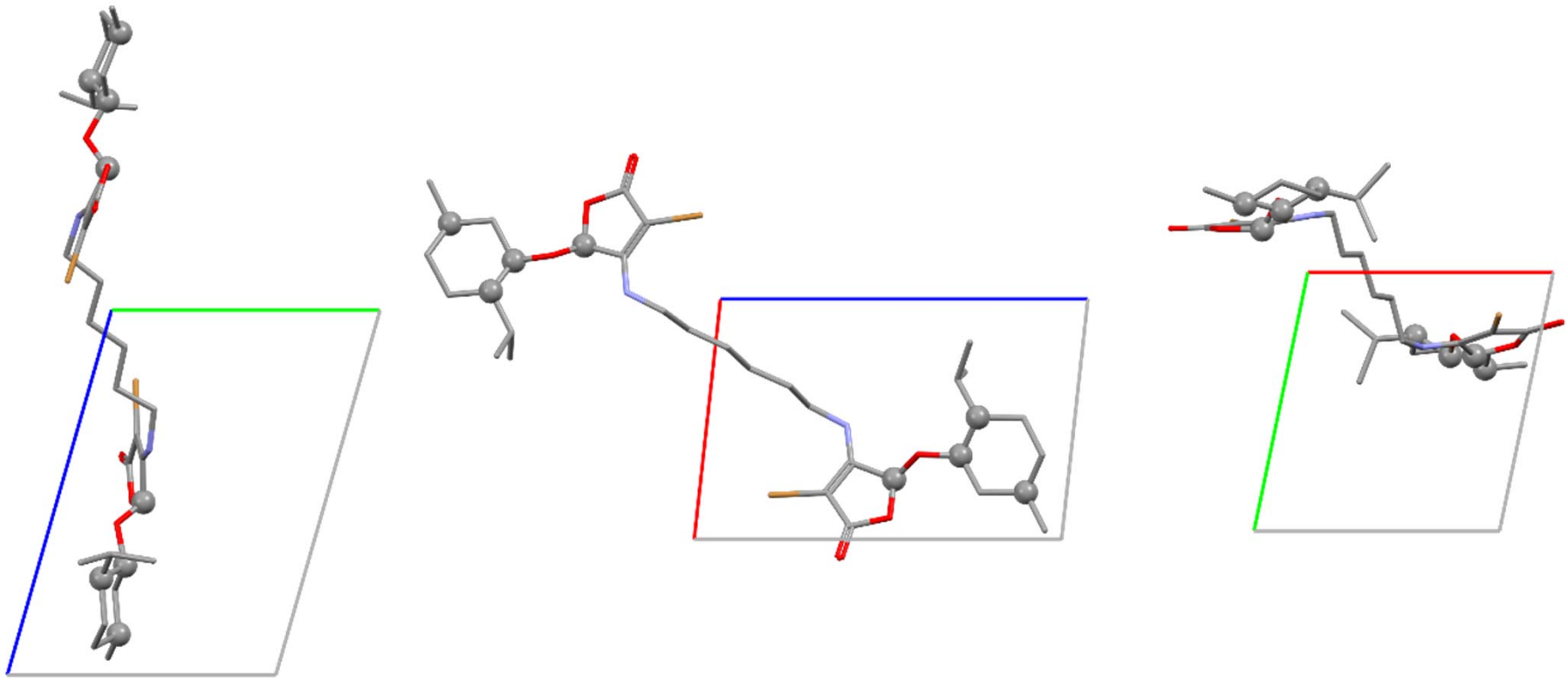


18 stereocenters; possible twofold symmetry;
disorder not shown

$P\bar{1}$ mimic

MODWAE
($P1$, Z=1)

Views along **a**, **b**, and **c**

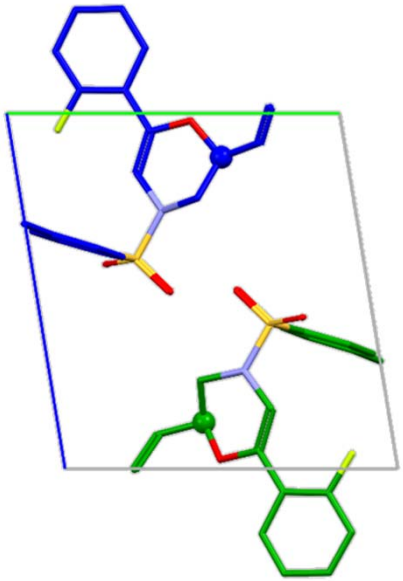


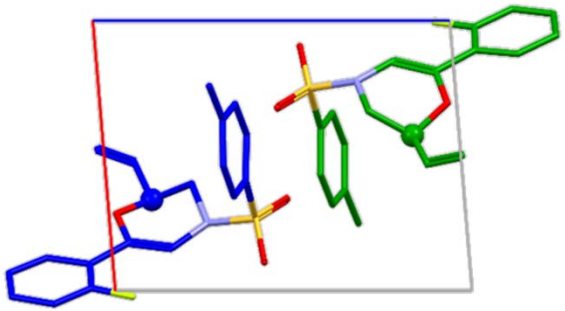
8 stereocenters; possible twofold symmetry

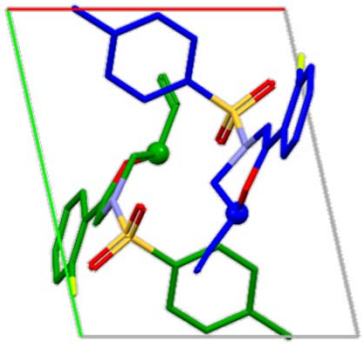
$P\bar{1}$ mimic

NIXDOQ
($P1$, Z=2)

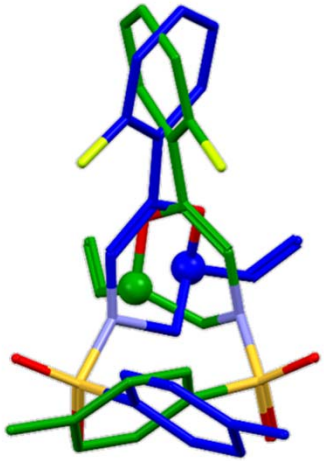
Views along **a**, **b**, and **c**



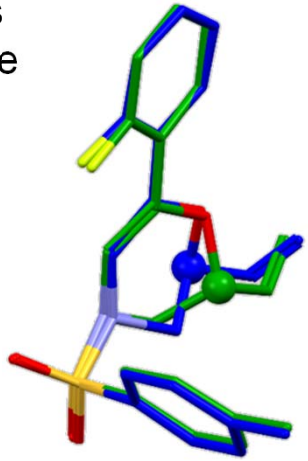




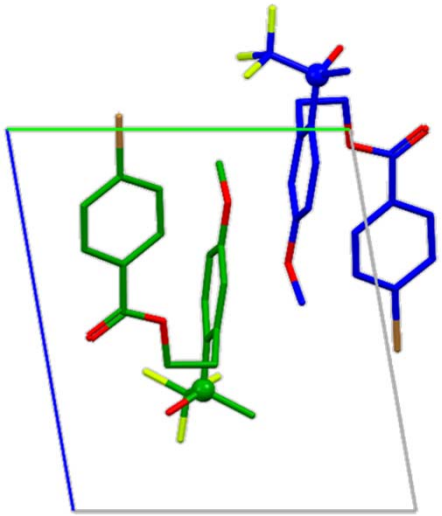
If the H and $CH{=}CH_2$ substituents at the one stereocenter were switched in half of the molecules they would be enantiomers



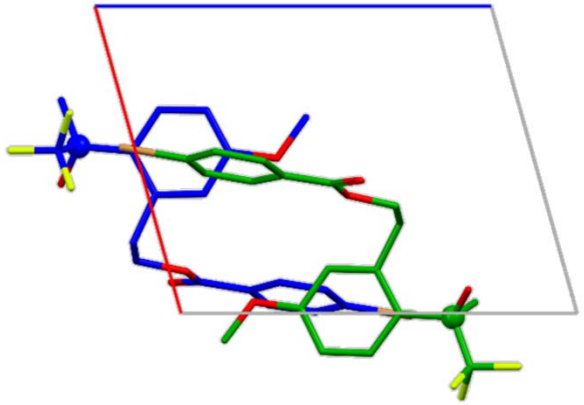
Best overlays of the two molecules as found and with one inverted



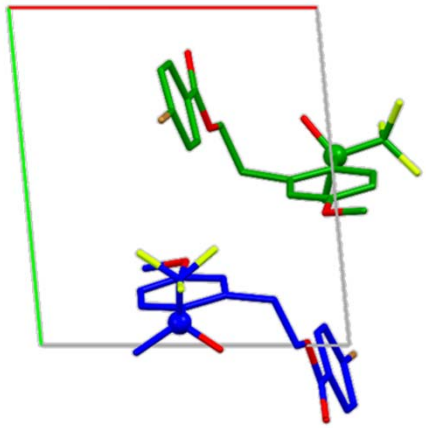
$P\bar{1}$ mimic



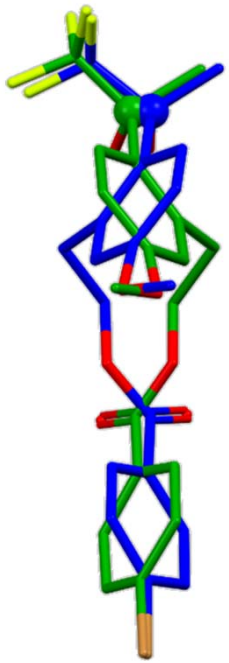
Views along **a**, **b**, and **c**



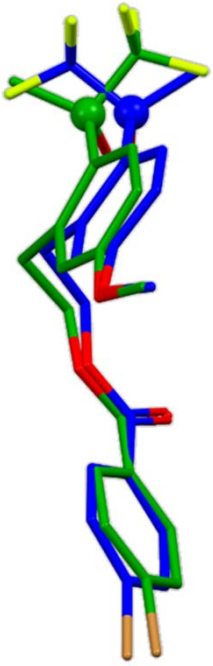
OKATID
(*P*1, *Z*=2)



If the CH_3 and CF_3 substituents at the one stereocenter were switched in half of the molecules they would be enantiomers



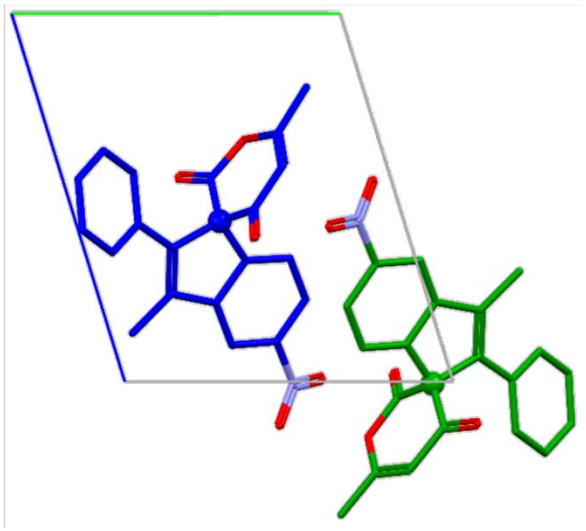
Best overlay of the two molecules as found and with one inverted

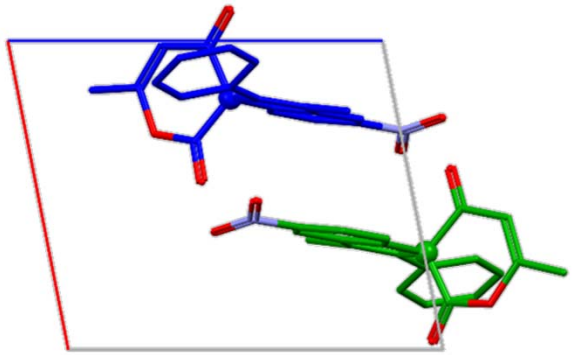


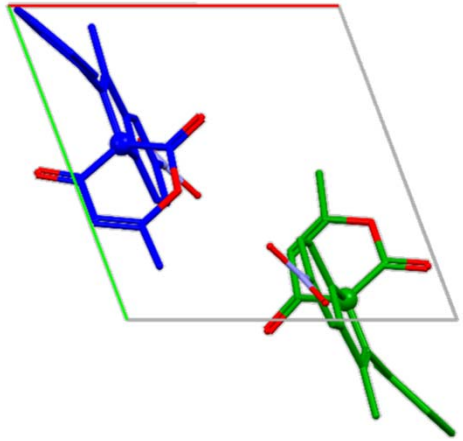
$P\bar{1}$ mimic

PACVEX
($P1$, Z=2)

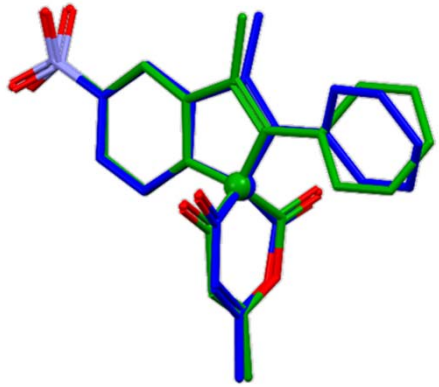
Views along **a**, **b**, and **c**







Best overlay of the two molecules as found



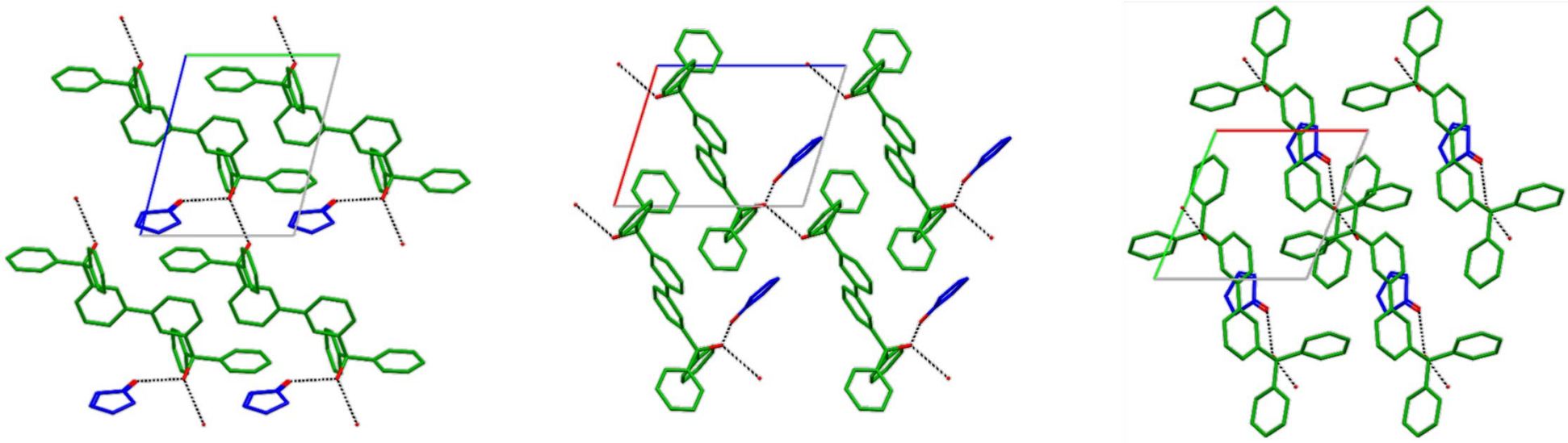
Except for the ring O atom the molecule has near mirror symmetry

PLATON issues no warning at all, even with increased tolerances
but the structure is #4 on the Rekis (2020) list of centrosymmetric mimics

Distorted $P\bar{1}$ (achiral)

PAPDER
(*P*1, *Z*=1)

Views along **a**, **b**, and **c**

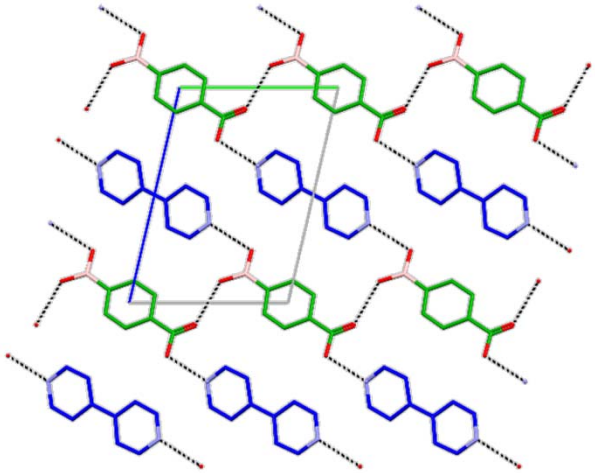


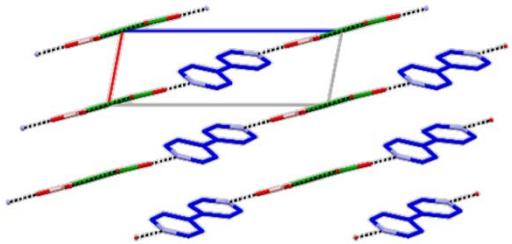
If the space group were $P\bar{1}$ with *Z'*=½ the cyclopent-2-en-1-one solvent molecule would have to lie on an inversion center and so could not participate fully in the OH…OH…O= H-bond motif. The structure was determined at 123 K so possibly there is disorder at a higher temperature

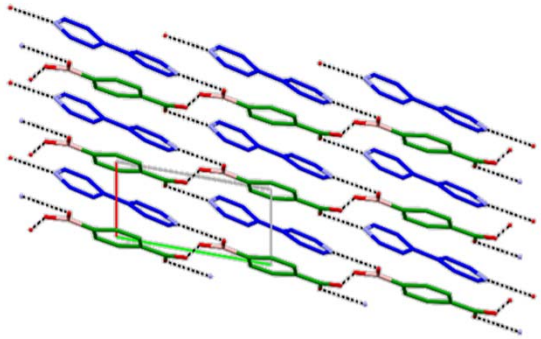
$P\bar{1}$ mimic

Views along **a**, **b**, and **c**

PAXTIS
(*P*1, *Z*=1)





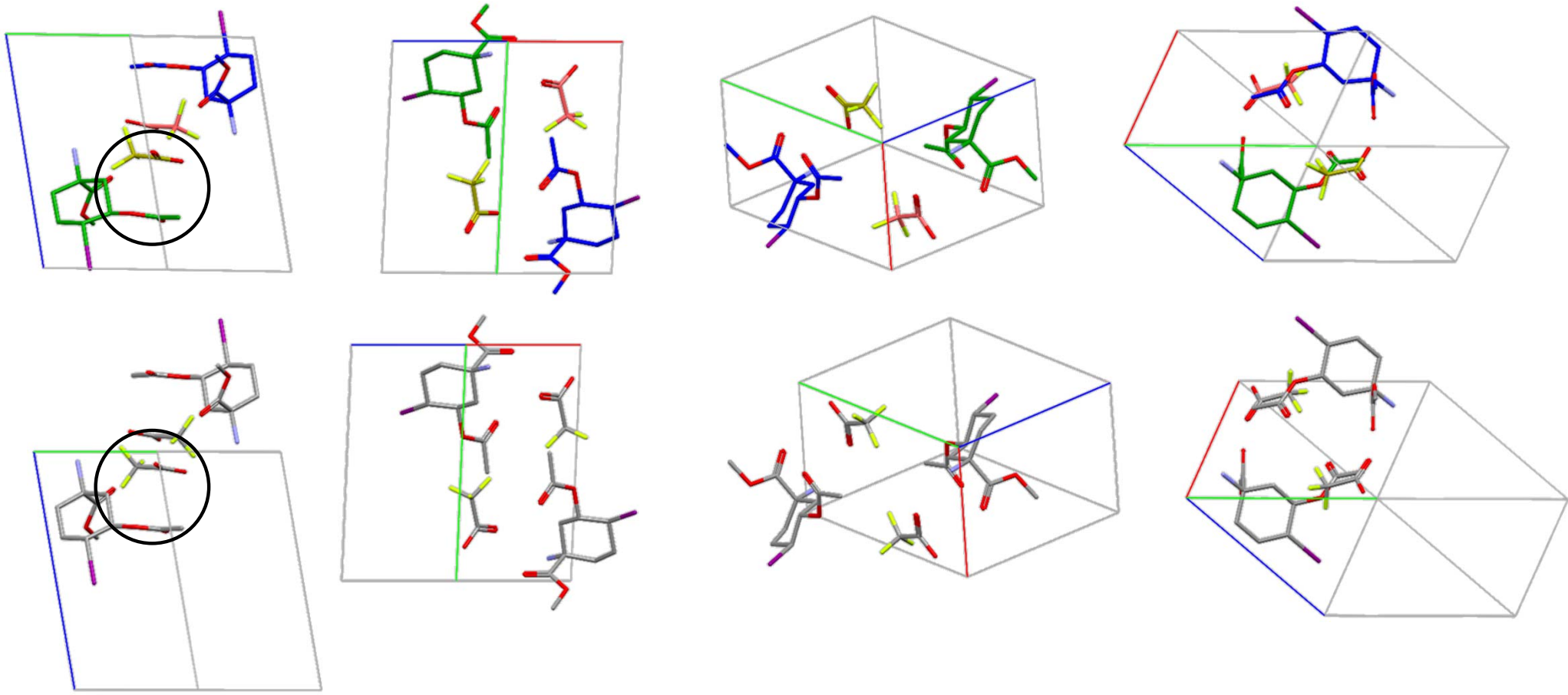


1:1 4-carboxybenzeneboronic acid 4,4'-bipyridine. The *para* C(=O)OH and $B(OH)_2$ substituents on the central benzene ring of the former form H bonds in very similar ways so that the B-containing molecule can mimic inversion symmetry

Distorted $P\bar{1}$ (a kryptoracemate)

RIGSEF
(*P*1, *Z*=2)

Views along [1$\bar{1}$0], [101]. [111]. and [1$\bar{1}$1]
as refined in *P*1 at RT (upper row) and as averaged in $P\bar{1}$ (lower row)



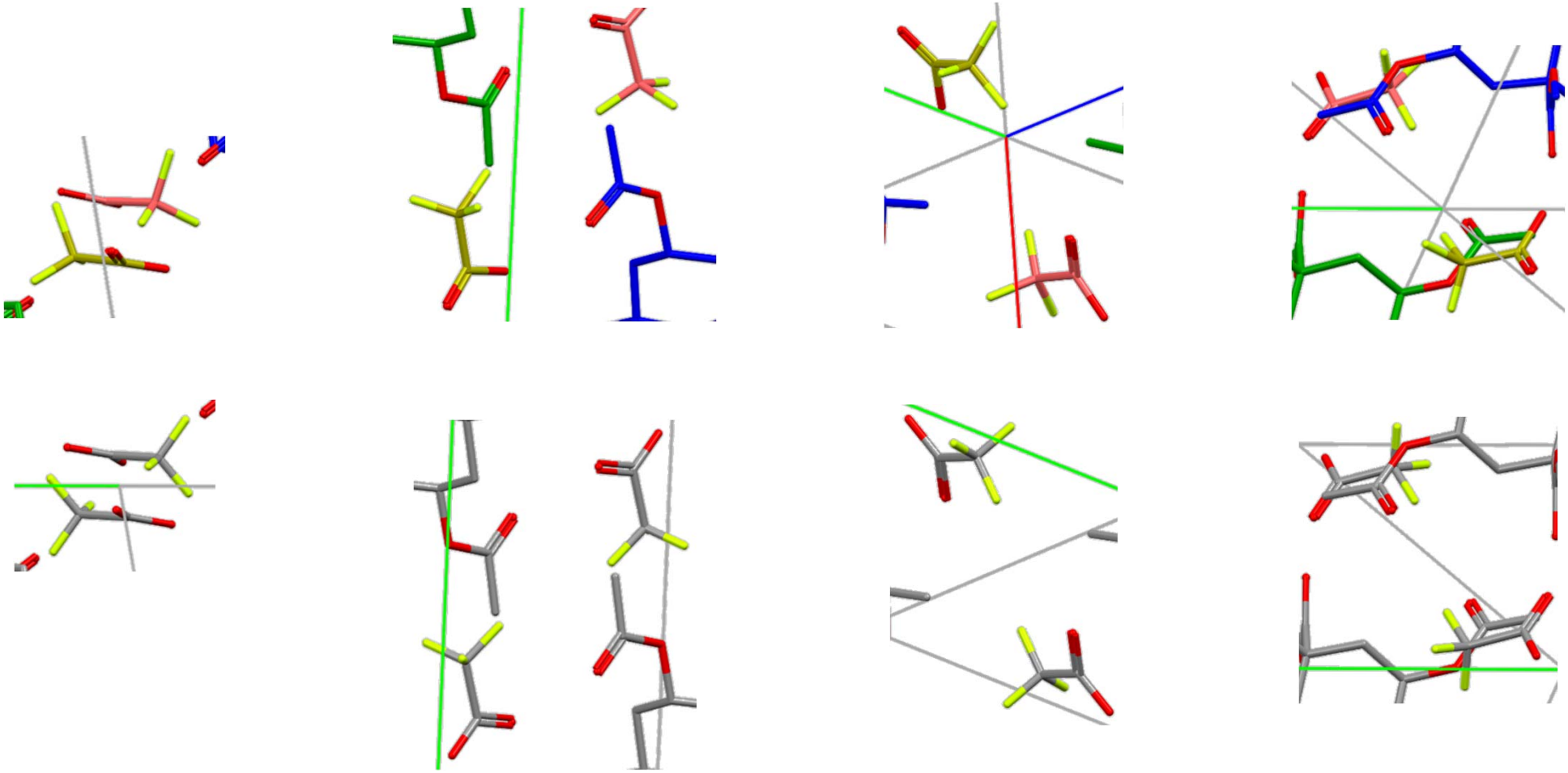
The $P\bar{1}$ averaging (Marsh, 1999) did not include a refinement. Most of the most perturbations from $P\bar{1}$ symmetry involve the F atoms but there are a number of other small differences as well. *PLATON* recommends $P\bar{1}$ but only at the 91% level

(see also next page)

Distorted $P\bar{1}$ (kryptoracemate)

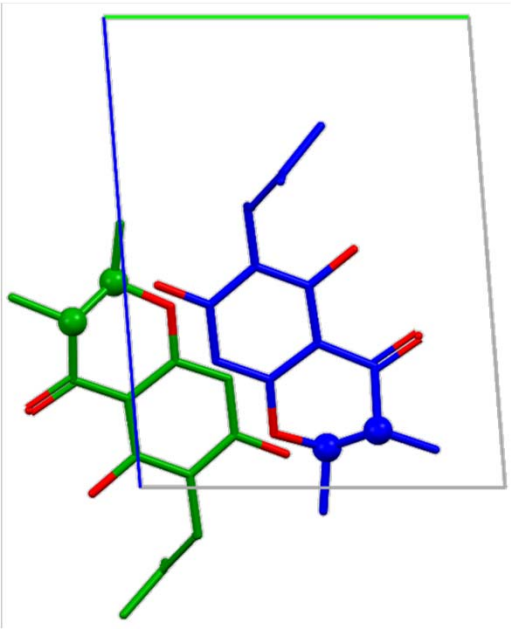
RIGSEF, con't ($P1$, Z=2)

Same views but cropped to show anions



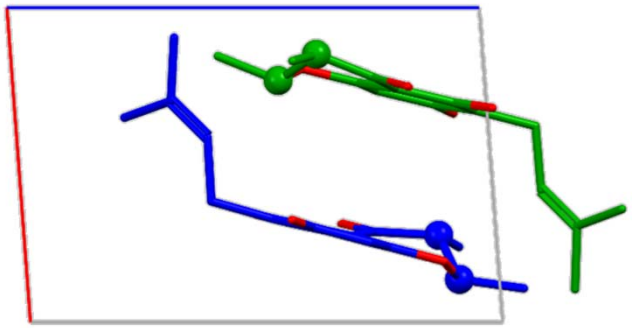
The F atoms in the $P1$ structure (R=0.041) may be somewhat disordered but there is no evidence they are as disordered as they would need to be in a $P\bar{1}$ structure

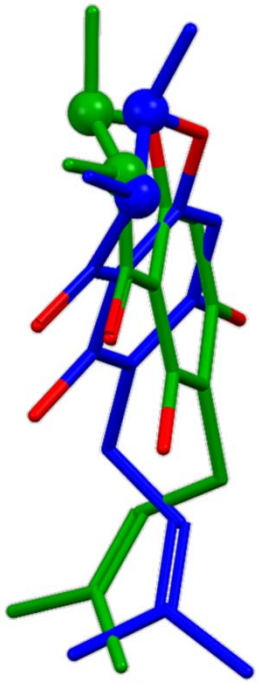
$P\bar{1}$ mimic



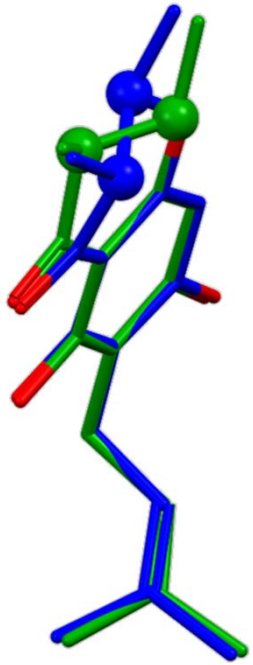
Two adjacent, homochiral -CHMe- stereocenters in a ring can mimic an inversion relationship very well

Views along **a**, **b**, and **c**

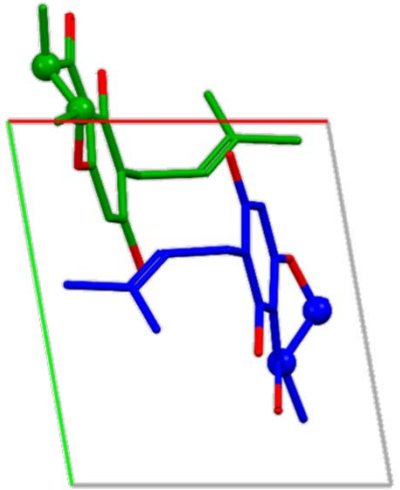




Best overlay of the two molecules as found and with one inverted



SUYLEF
(*P*1, *Z*=2)

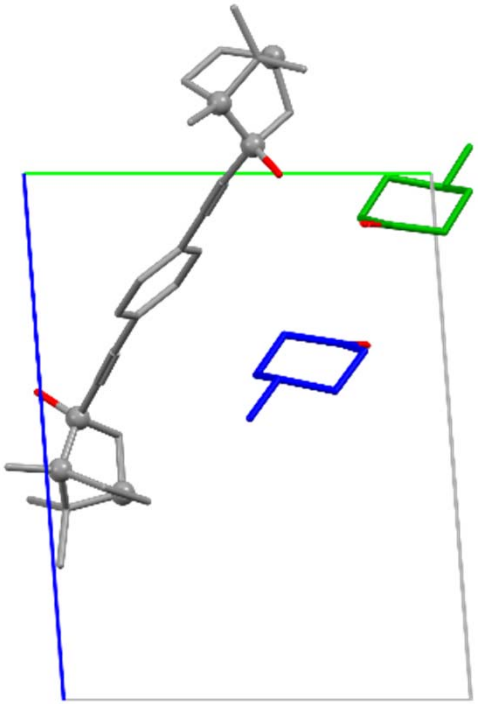


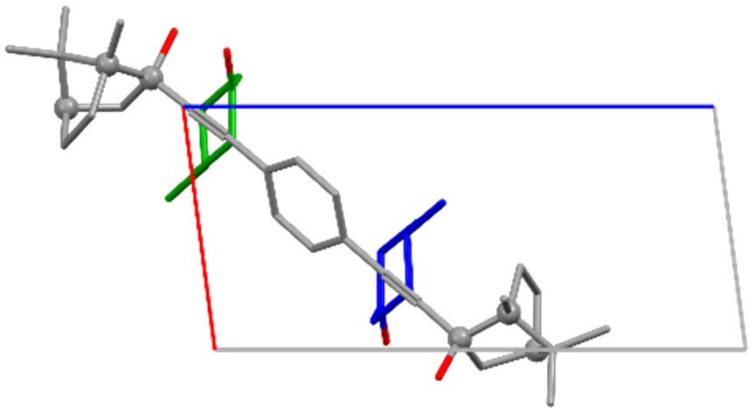
$P\bar{1}$ mimic

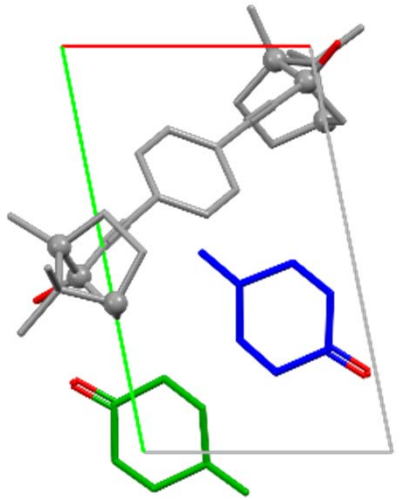
Views along **a**, **b**, and **c**

TUHWAW
(*P*1, *Z*=1)

1:2 solvate
(4-methylcyclo-
hexanone)





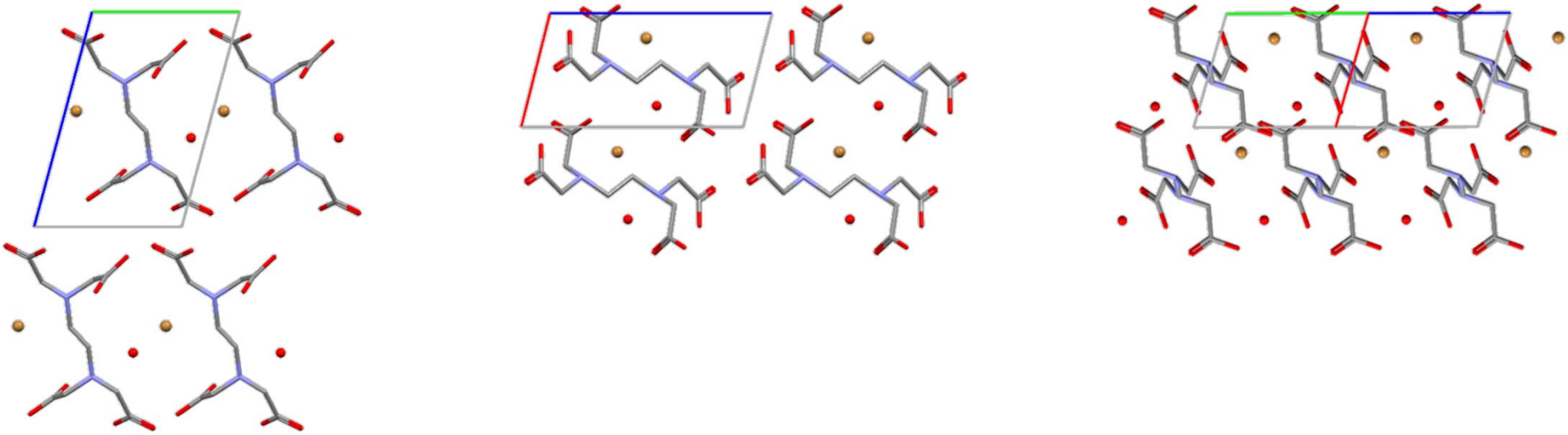


6 stereocenters; possible twofold symmetry

$P\bar{1}$ mimic

Views along **a**, **b**, and [011]

VEYXAY
(*P*1, *Z*=1)

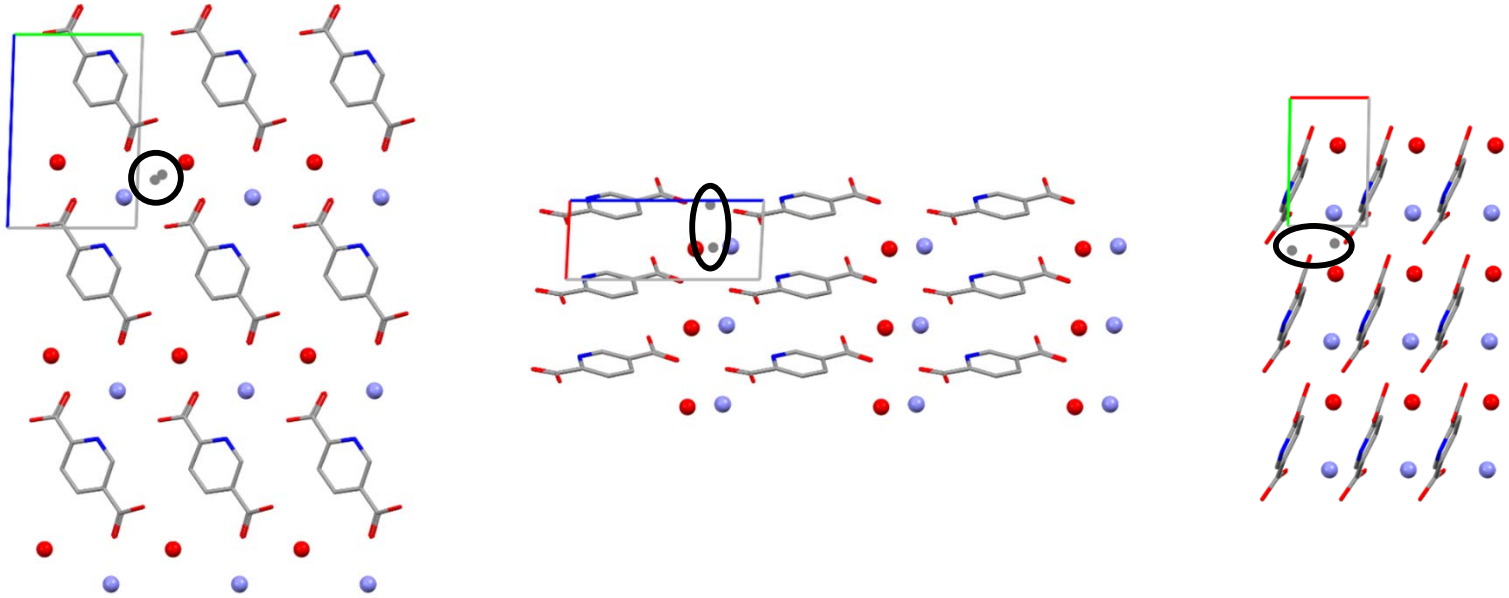


The cation of EDTA hydrobromide monohydrate has excellent inversion symmetry but the inversion centers of a $P\bar{1}$ description would relate the Br^- ion and water molecule. Their positions are well related by the approximate symmetry but chemically they are very different. (No displacement ellipsoids are available but a significant Br^-/H_2O disorder would have raised the *R* factor above 0.050.)

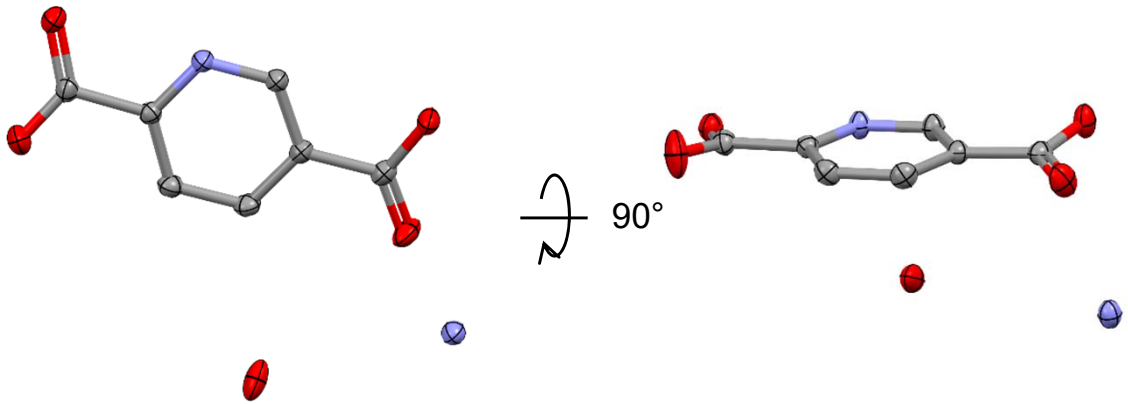
$P\bar{1}$ mimic

VIHTUD
($P1$, Z=1)

Views along **a**, **b**, and **c**

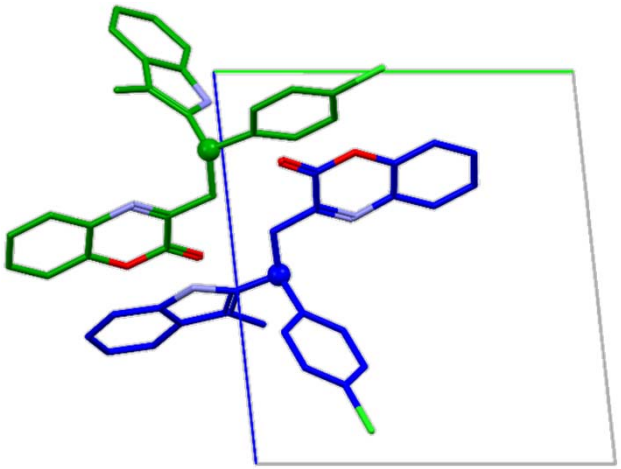


The ammonium salt hydrate of 5-carboxypyridine-2-carboxylate. Centroids between two cations related by translation and for the cation and water molecule are shown.

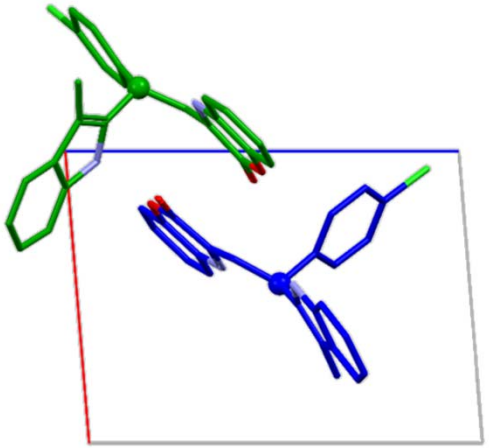


The displacement ellipsoids suggest some disorder of the water molecule and perhaps the NH_4^+ ion is possible but there does not seem to be any disorder in the C_5N ring

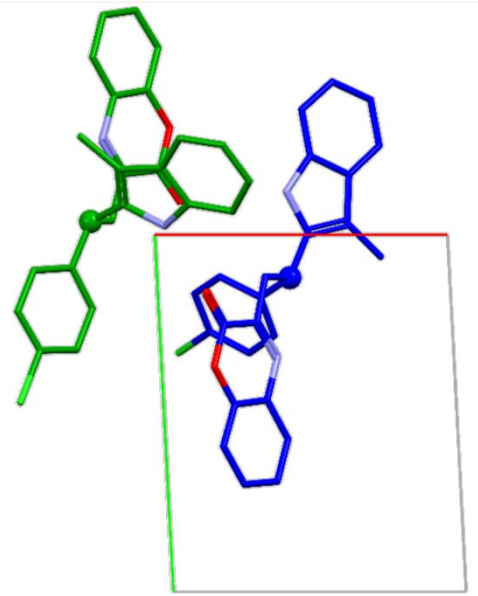
$P\bar{1}$ mimic



Views along **a**, **b**, and **c**

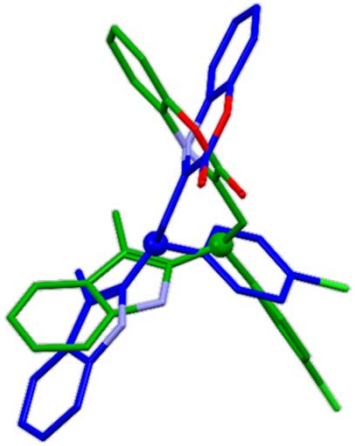


XOZSIQ
(*P*1, *Z*=2)



A $P\bar{1}$ mimic requires inversion relationship of 4-chlorophenyl and 3-methyl-1H-indol-2-yl)ethyl substituents, but they are both planar and are similar in size. The approximate inversion mimicry is convincing.
Two long (3.09, 3.31 Å) NH…O= bonds connect the two molecules shown.
The two molecules have very different conformations

Best overlay of the two molecules as found

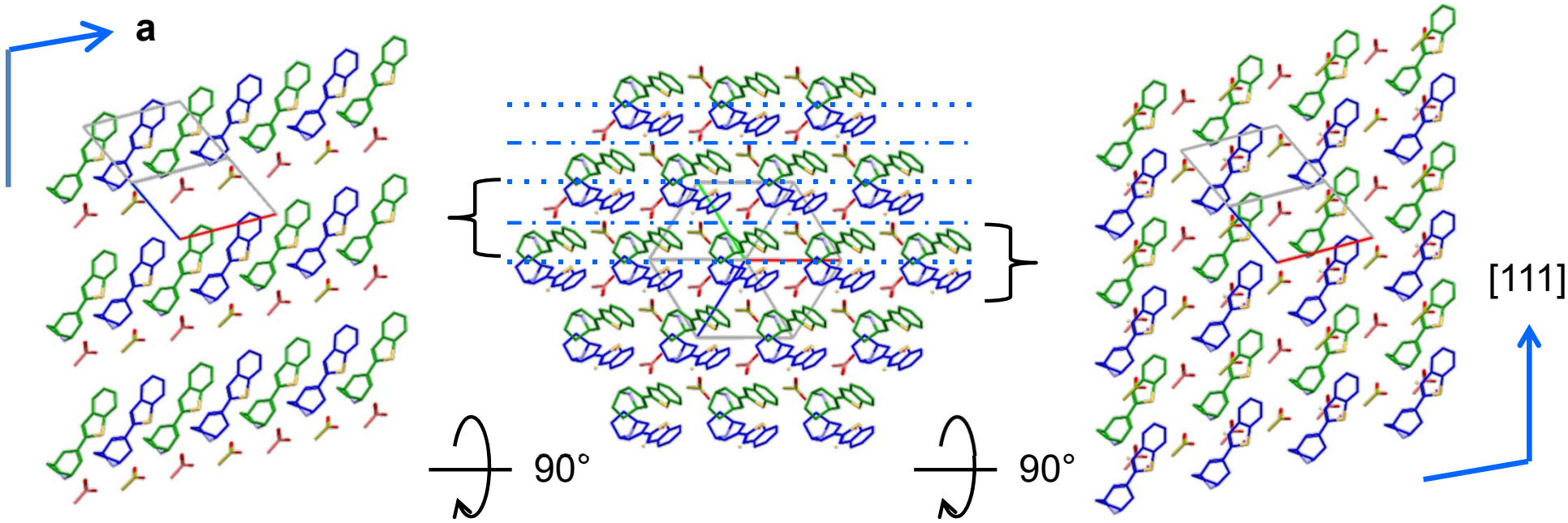


Structures that have approximate glide symmetry
by distortion and by mimicry

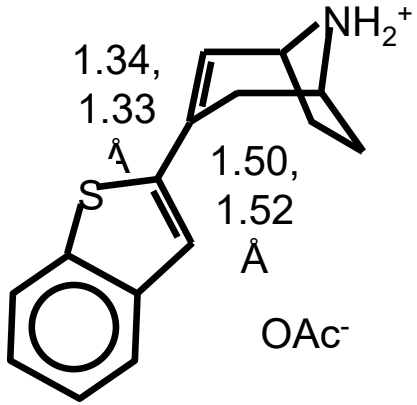
glide mimic (*Ia*), 3-D [the mirror is $(01\bar{1})$]

MEDNAM
(*P*1, *Z*=2)

Projection along [111]



The glides along **a** and [111] would switch the single and double bonds in the 8-azoniabicyclo[3.2.1] substituent but the lengths are clearly not the same

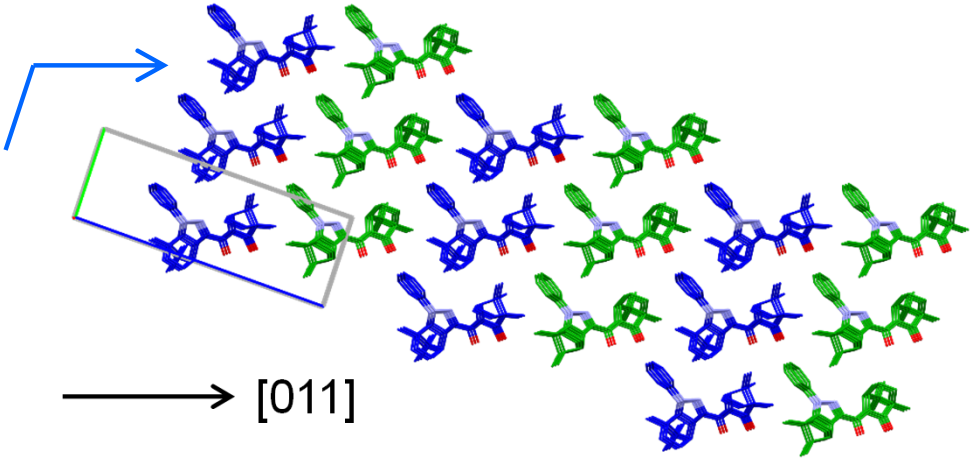


Ia, *Z*=4, *Z'*=1
axes [111], $[01\bar{1}]$, $[\bar{1}00]$;
angles 90.0, 104.7, 90.2°

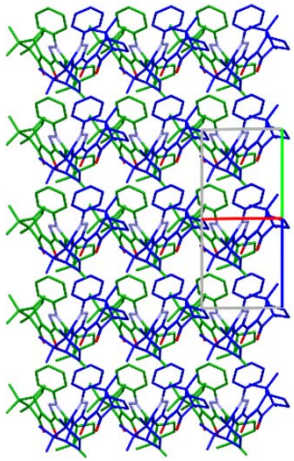
glide mimic (*Pn* with **a** unique), 3-D

UQEVIX
(*P*1, *Z*=2)

View along **a***



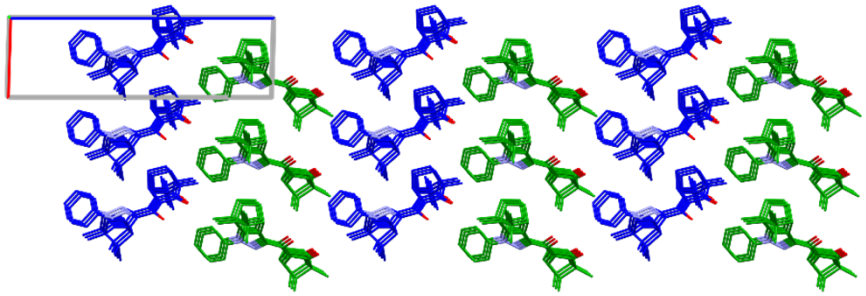
90°



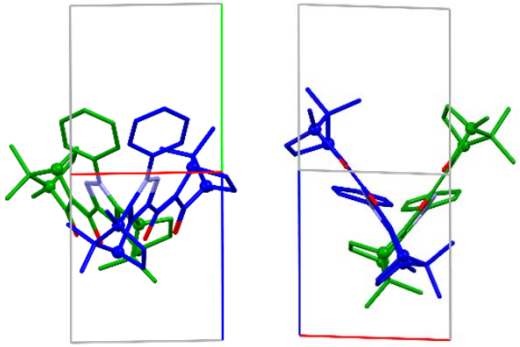
[100]

View along **b***

Cell angles are
91.5, 91.7, 91.4°



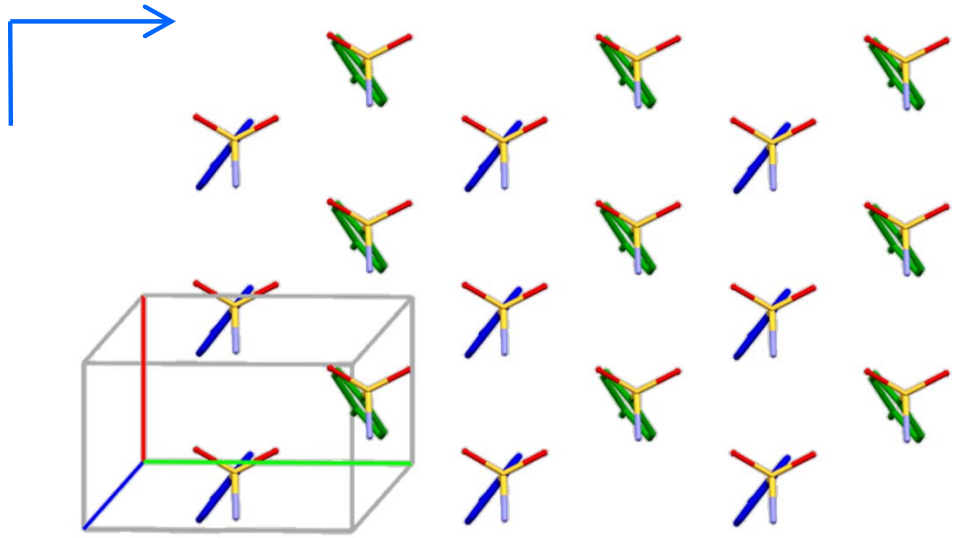
Views along [011] and [01$\bar{1}$]
showing the glide mimicry



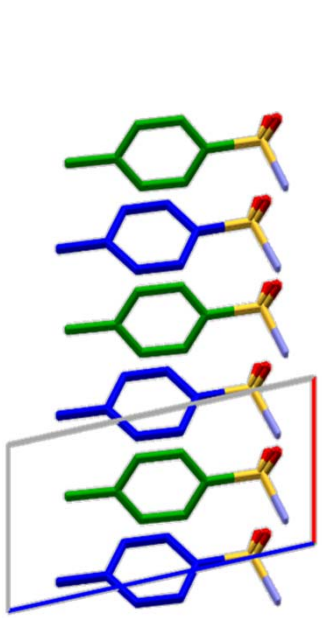
distorted glide (*pb*11), 2-D (achiral)

KUSVEZ03
(*P*1, *Z*=2)

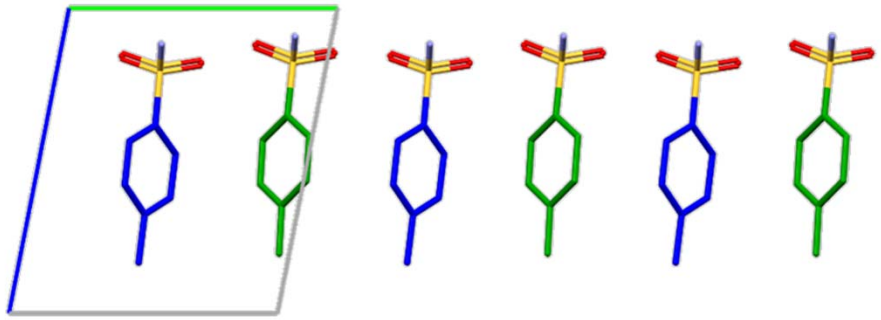
View along **c***



90°



90°



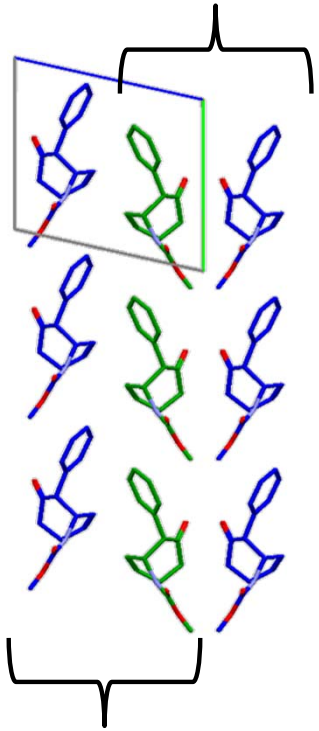
Layer (001)
*pb*11, *z*=2, *z'*=1
axes [010], [100]

distorted glide (*p*11*a*), 2-D (kryptoracemate)

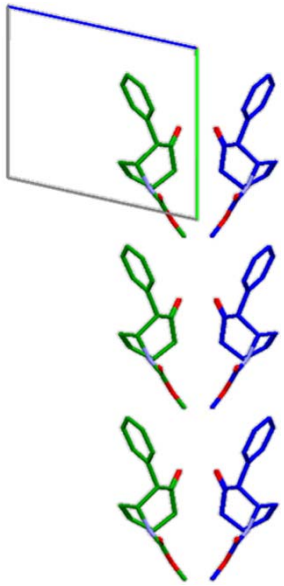
XEFNAX
(*P*1, *Z*=2)

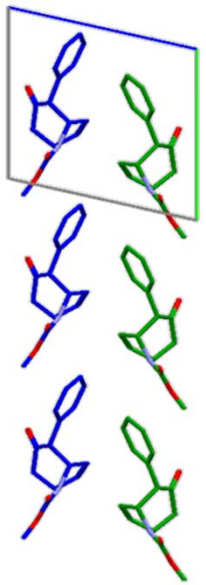
Views along **a**

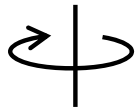
Approximate
symmetry
*p*11*a*



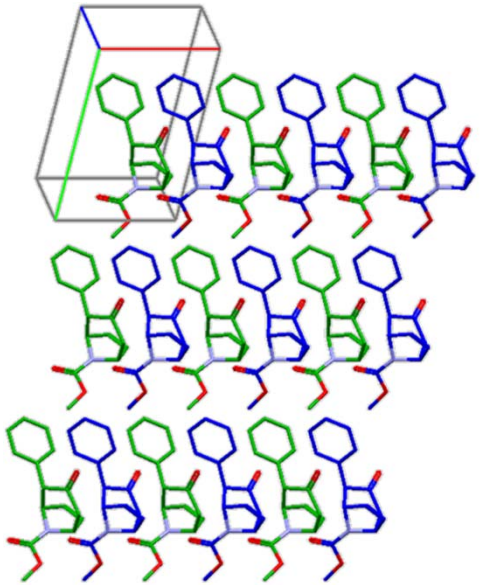
(no
approximate
symmetry)

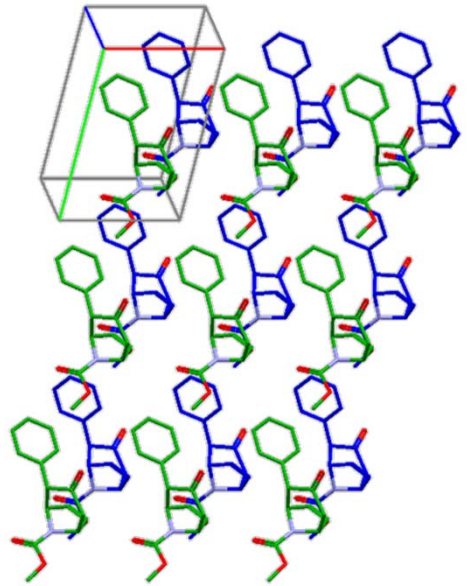






90°



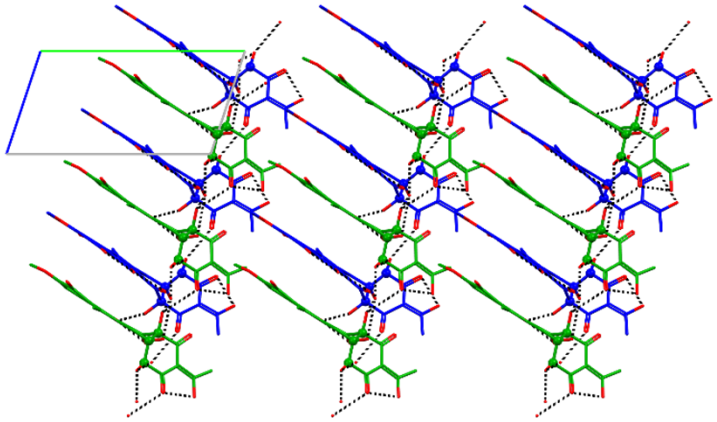


Layer (001)
*p*11*a*, *z*=2, *z'*=1
axes [100], [010]

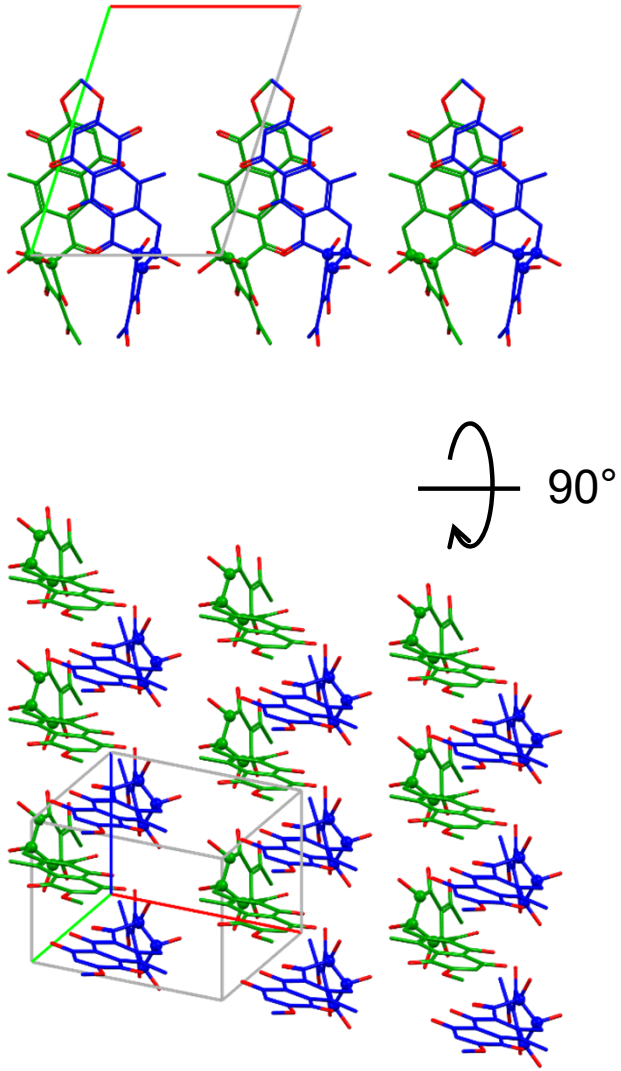
glide mimic, 1-D

CEGPIN
(*P*1, *Z*=2)

View along **a**
(H bonds shown in this view only)



Layer (010)



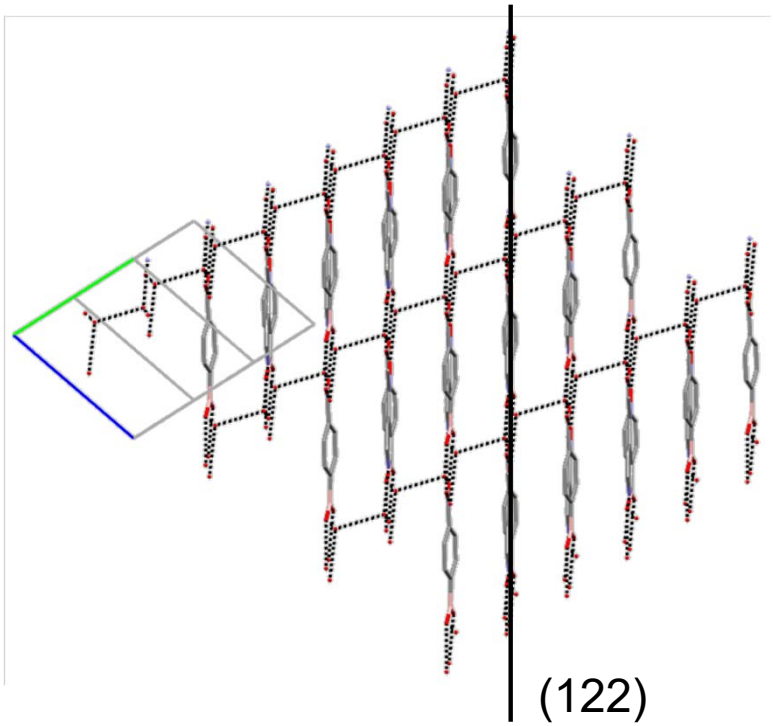
H-bonded columns [001] have very good approximate glide symmetry but the offset along **a** is not correct for either *pb*11 or *cm*11 approximate symmetry

Structures that have an approximate mirror

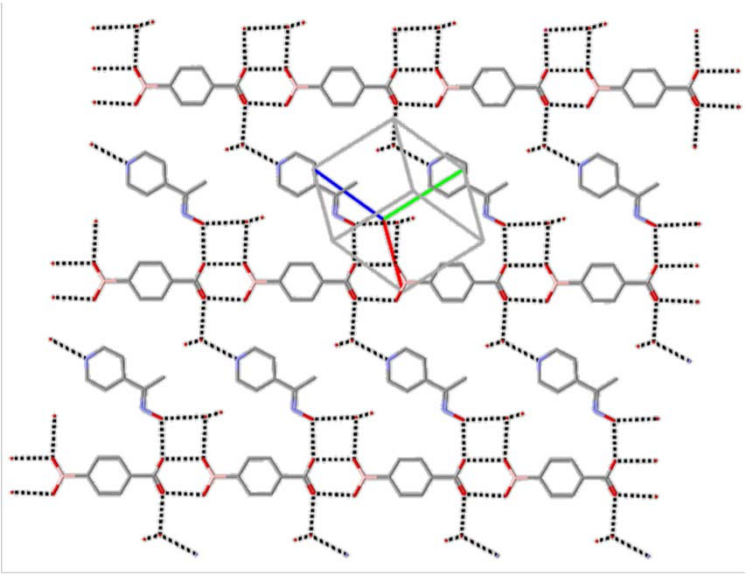
distorted *p*11*m*, *z'*=½, 2-D (achiral)

FETDIS
(*P*1, *Z*=1)

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



Layer (122)



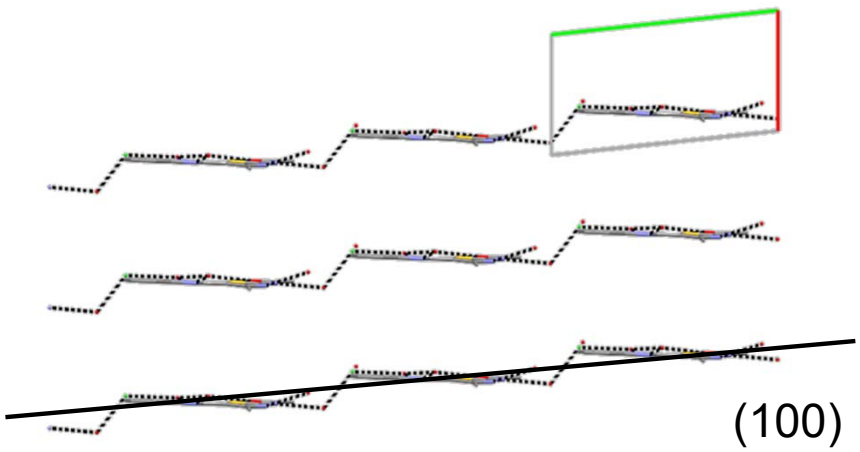
*p*11*m*, *z*=1, *z'*=½
or even *p*112/*m*, *z*=1, *z'*=¼

1:1:2 hydrated salt;
an H bond between the water molecules
links the H-bonded layers

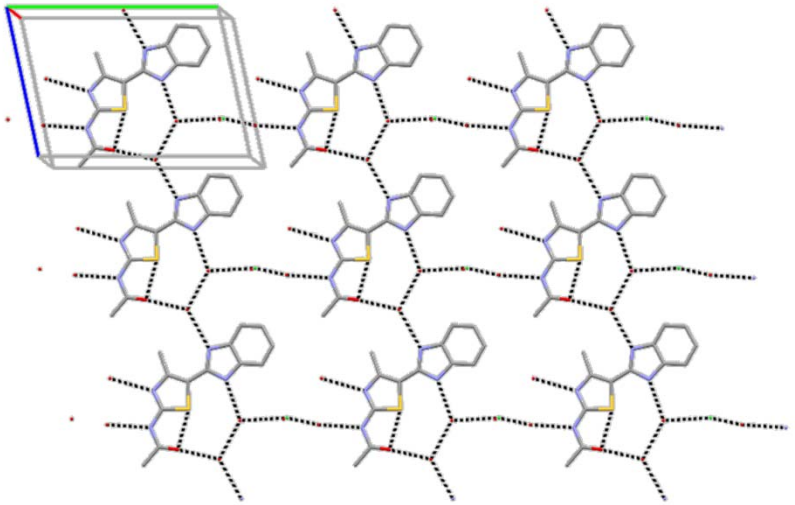
distorted *p*11*m*, *z'*=½, 2-D (achiral)

HOCYAZ
(*P*1, *Z*=1)

View along [001]



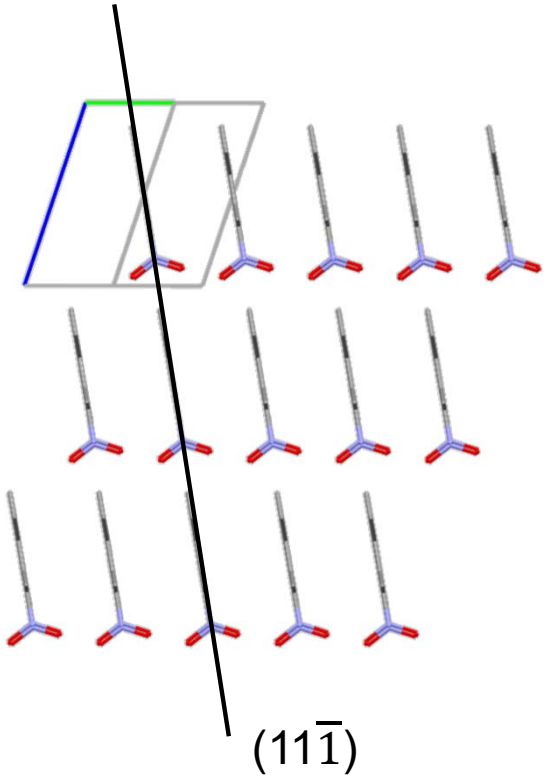
Layer (100)



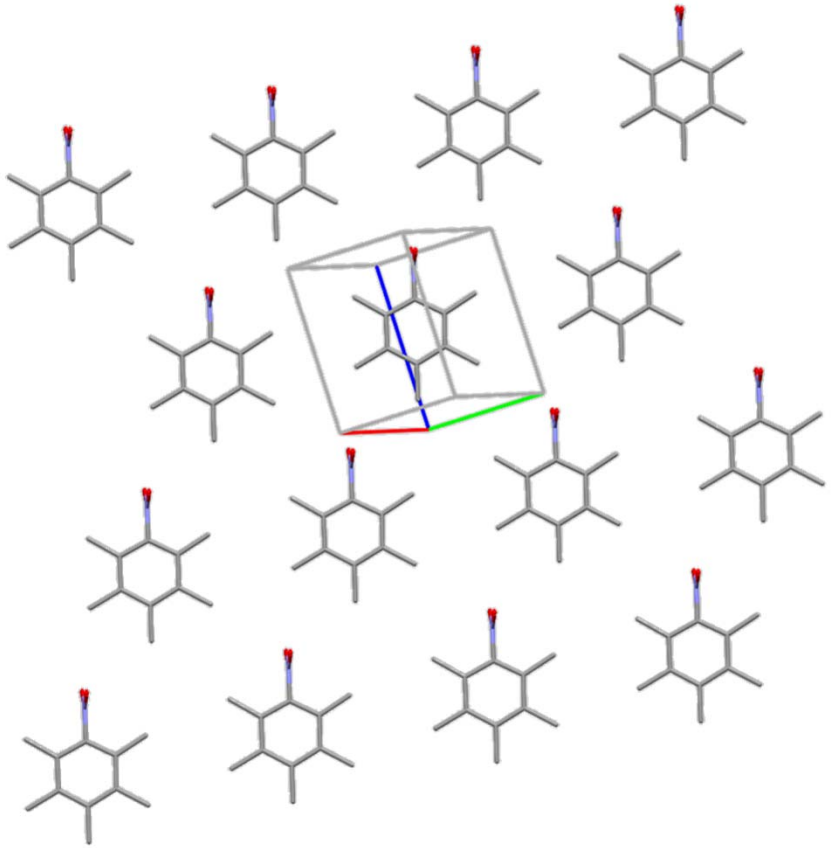
distorted *p*11*m*, *z'*=½, 2-D (achiral)

PMNTBZ01
(*P*1, *Z*=1)

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



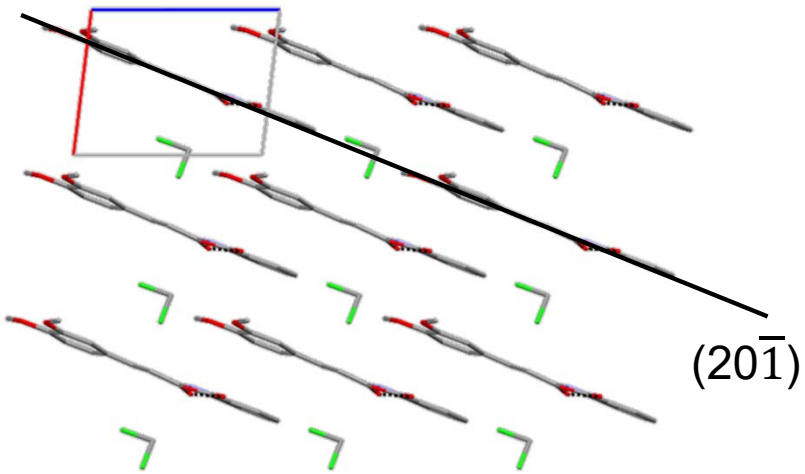
Layer $(11\bar{1})$



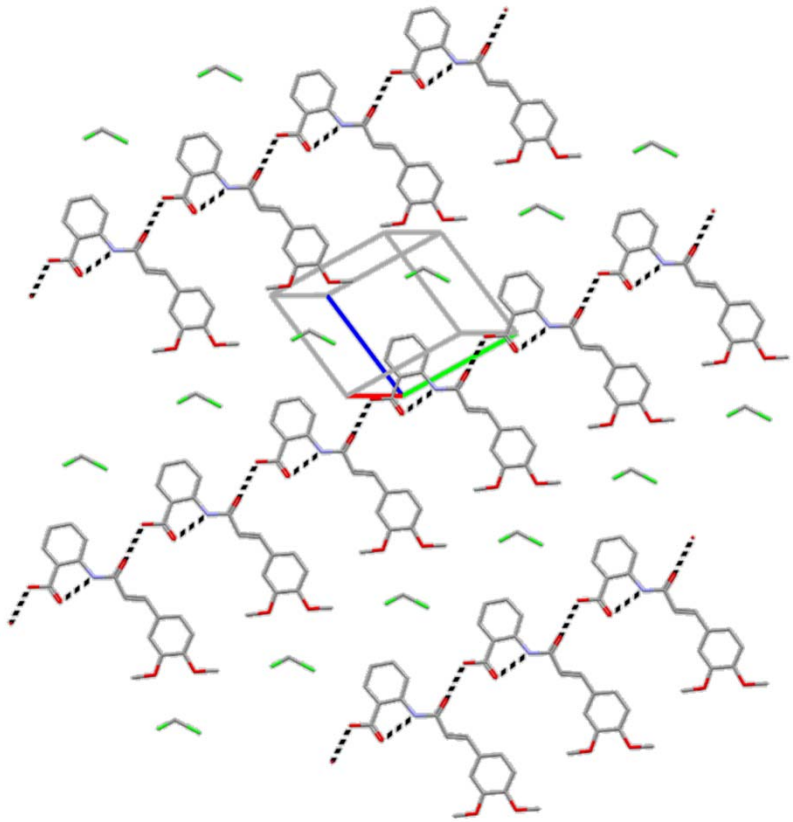
distorted *p*11*m*, *z'*=½, 2-D (achiral)

YALWIS
(*P*1, *Z*=1)

View along [010]



Layer (20$\bar{1}$)

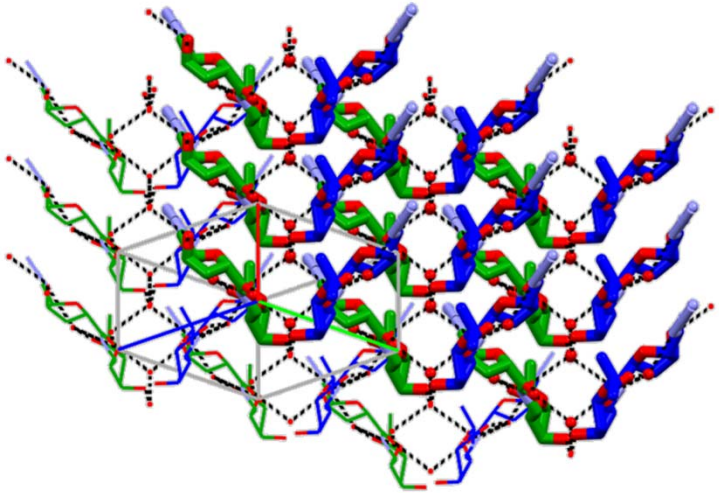


Structures that have approximate symmetry *C*2 or *c*211

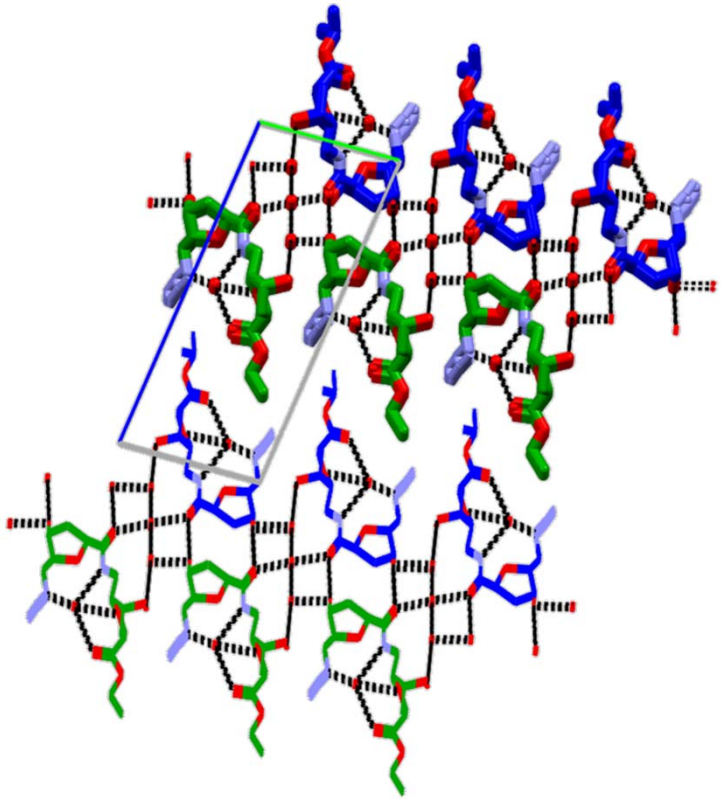
2&2$_1$, 3-D

CIQFOY
(*P*1, *Z*=2)

View along [111];
a is vertical



90°

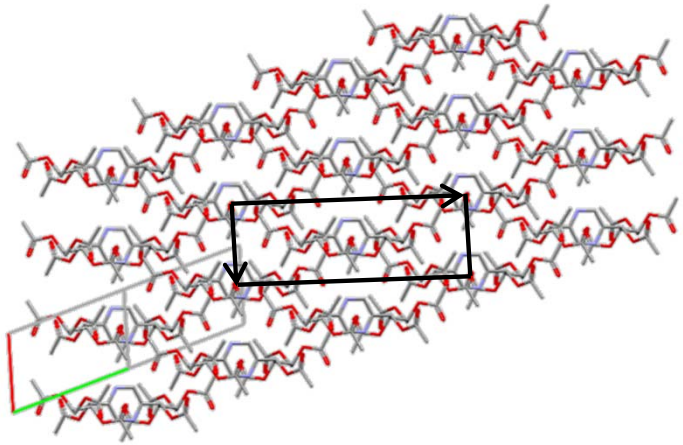


*C*211, *Z*=4, *Z'*=1
axes [120], [100], [$\overline{1}\overline{1}\overline{1}$],
angles 91.6, 96.3, and 89.9°

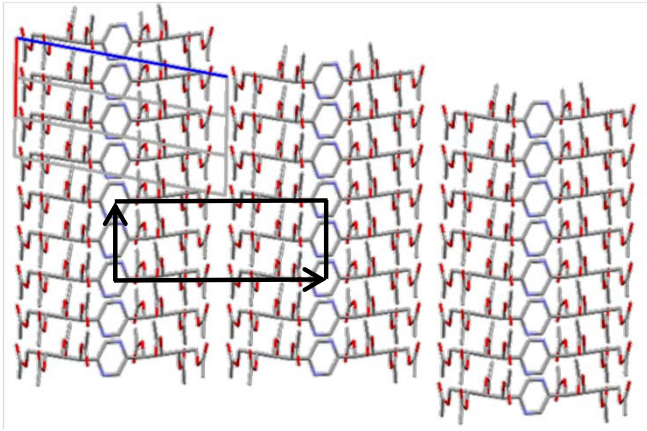
2&2$_1$ mimic, 3-D

SITFEH
(*P*1, *Z*=1)

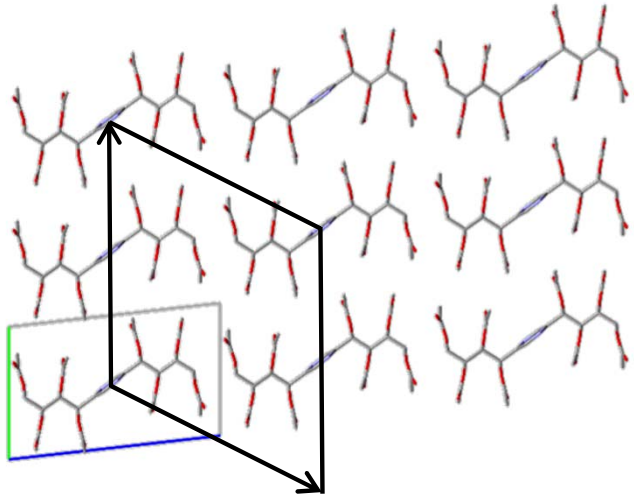
View along [0$\bar{1}$1]



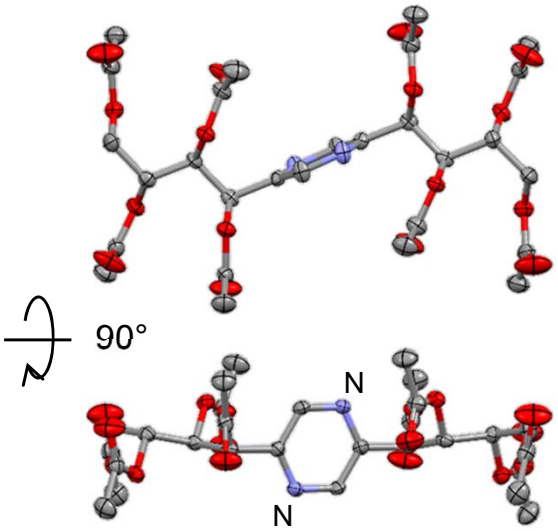
View along [$\bar{1}$20]



View along [$\bar{1}$00]



*C*2, *Z*=2, *Z'*= ½
axes [$\bar{1}$20], [$\bar{1}$00], [0$\bar{1}$1]
angles 89.3, 117.2, 89.3°



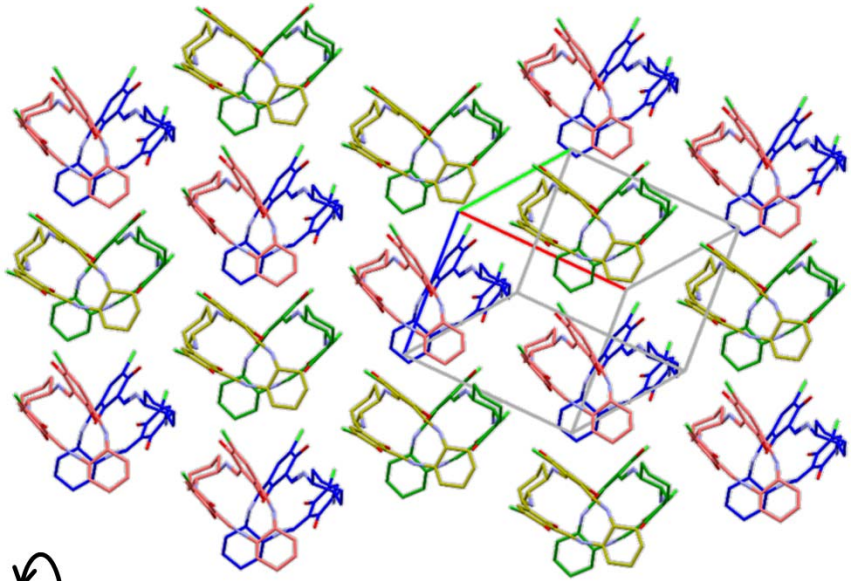
The two N atoms break the approximate twofold symmetry. At 159 K there is no indication of any disorder.

2&2$_1$ plus, 3-D

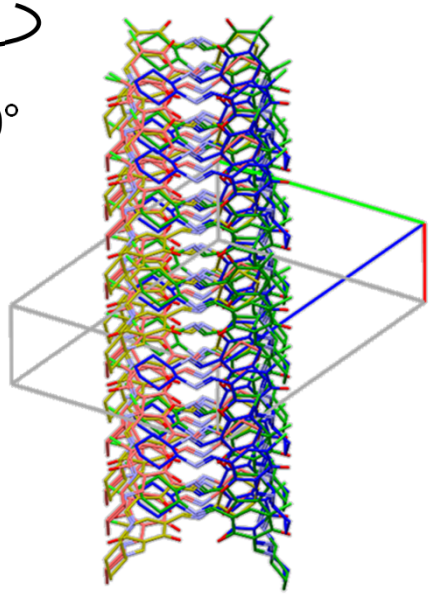
(while there are obvious layers the approximate symmetry is actually 3-D; see next page)

XEVCEJ
(*P*1, *Z*=4)

View of a layer (011)

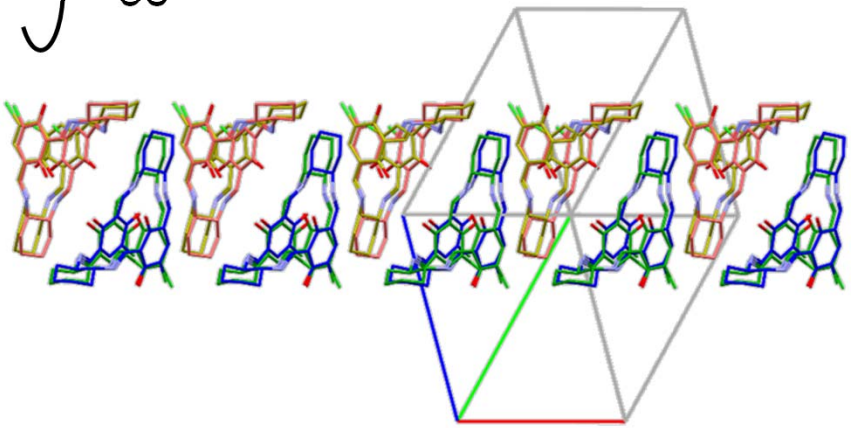


90°



The two independent EtOHs and the disordered H_2Os (6? 7?) are not shown; all H bonds involve solvent and lie within the layer

90°



Layer (011)
*c*211, *z*=4, *z'*=1
axes [$\frac{3}{2}\frac{1}{2}\overline{\frac{1}{2}}$], [$\overline{\frac{1}{2}}\ \frac{1}{2}\overline{\frac{1}{2}}$]

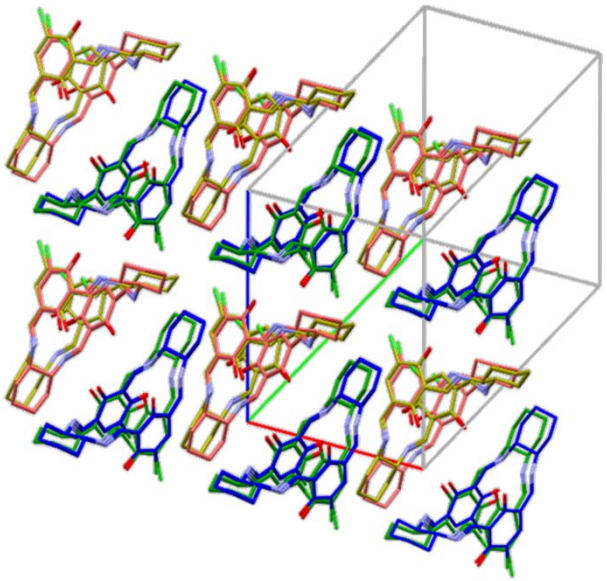
The approximate translations are [111]/2 plus any lattice vector *leg*, [$\bar{1}$11]/2, [1$\bar{1}$1]/2, *etc*)

(see also next page)

2&2$_1$ plus, 3-D

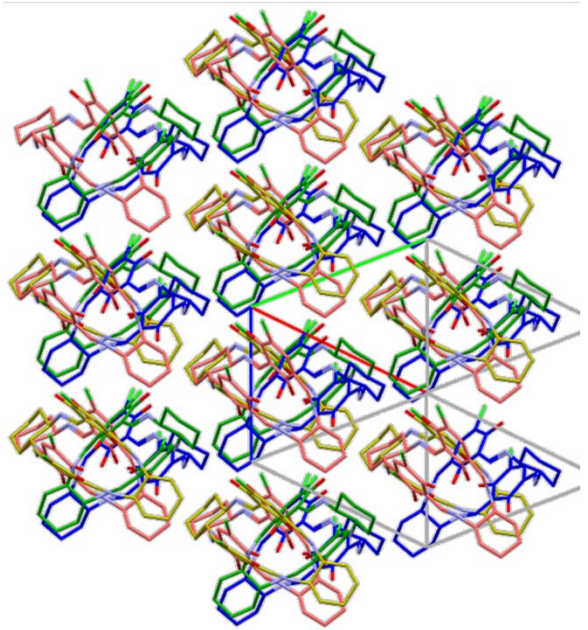
XEVCEJ, con't (*P*1, *Z*=4)

View along [1$\bar{1}$1]



90.4°

View along [$\bar{1}$11]



The two independent EtOHs and the disordered H_2Os (6? 7?) are not shown; all H bonds involve solvent and lie within layers (011)

*C*2, *Z*=4, *Z'*=1

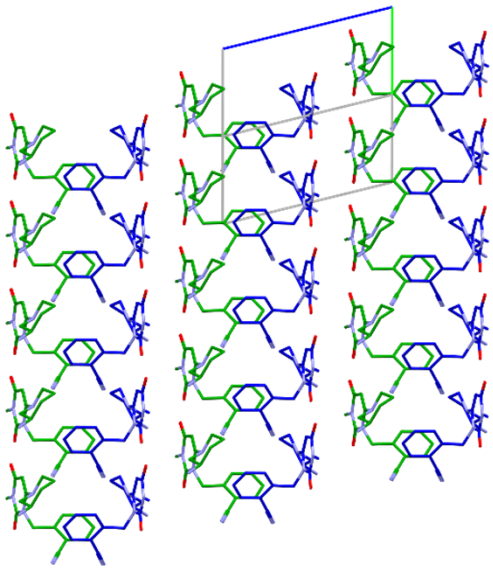
axes [$\frac{3}{2}\frac{1}{2}\bar{\frac{1}{2}}$], [$\bar{\frac{1}{2}}\ \frac{1}{2}\bar{\frac{1}{2}}$], [$\bar{\frac{1}{2}}\frac{1}{2}\frac{1}{2}$]

The approximate translations are [111]/2 plus any lattice vector (*eg*, [$\bar{1}$11]/2, [1$\bar{1}$1]/2, *etc*)

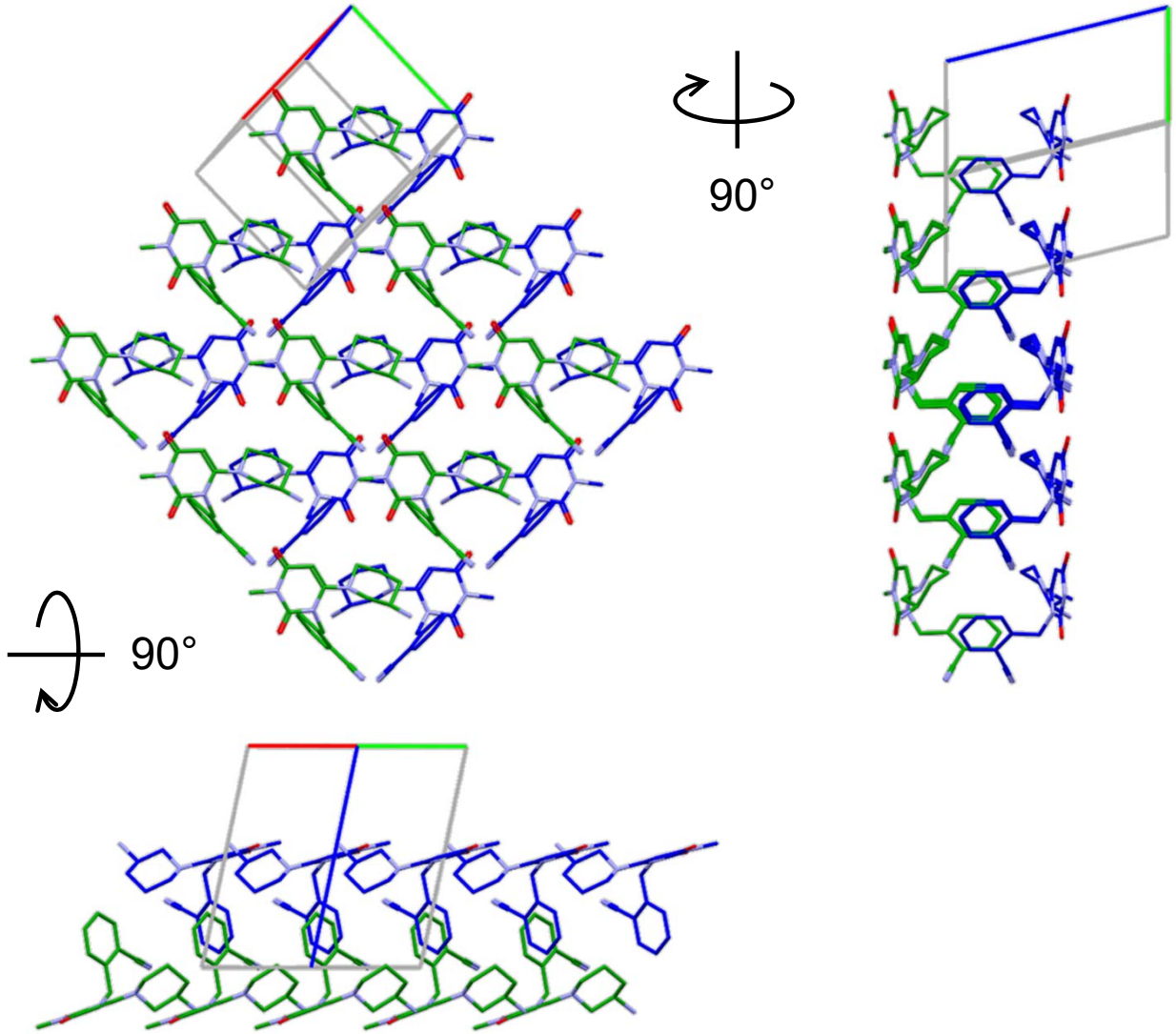
2&2$_1$, 2-D

BILJIR01
(*P*1, *Z*=2)

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



Layer (001), ½ < *z* < 1½



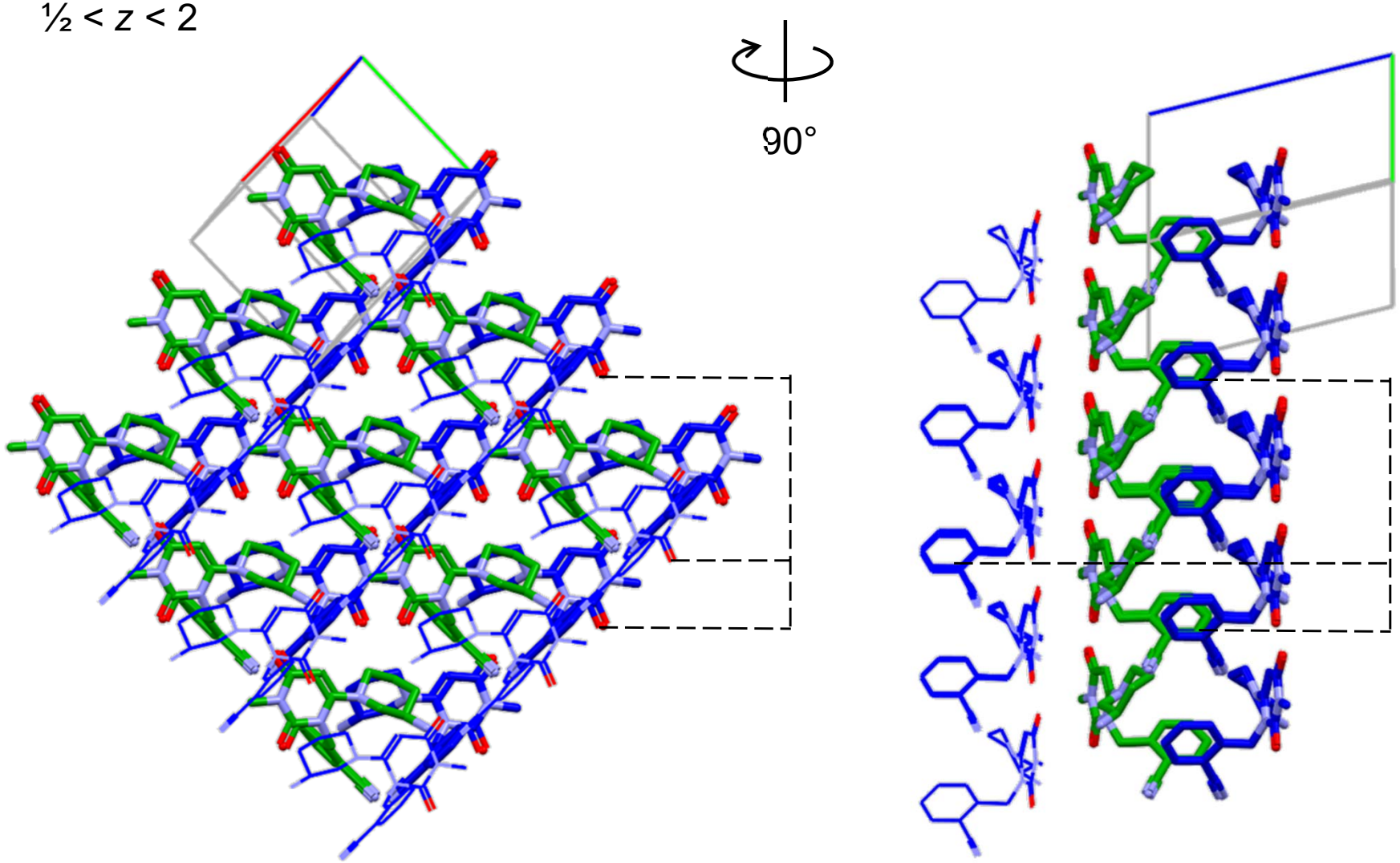
(see also next page)

2&2_1, 2-D

The layers (001) are offset by approximately [110]/4

BILJIR01, con't (*P*1, *Z*=2)

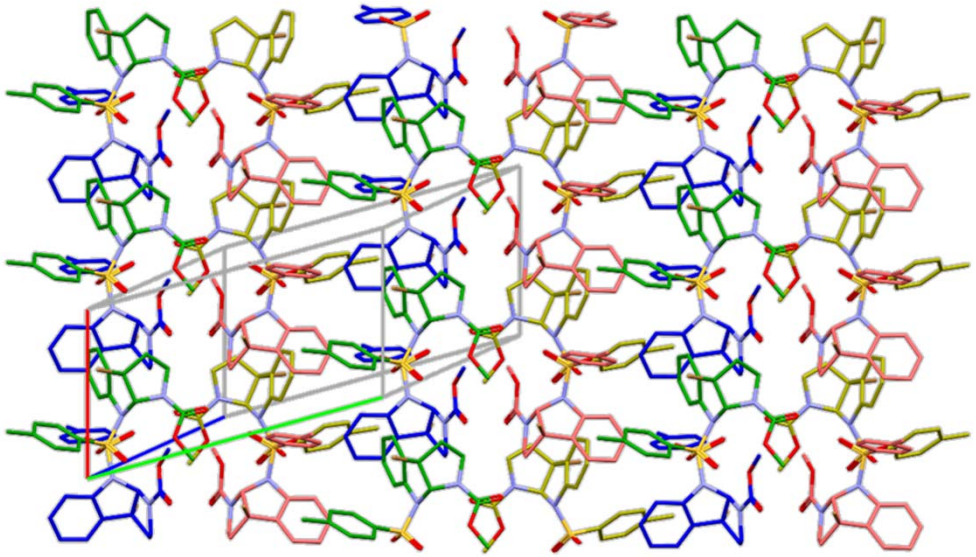
1.5 layers (001), ½ < *z* < 2



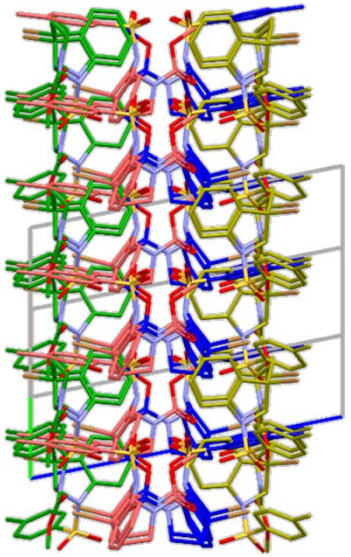
2&2$_1$, 2-D

BISREC
(*P*1, *Z*=4)

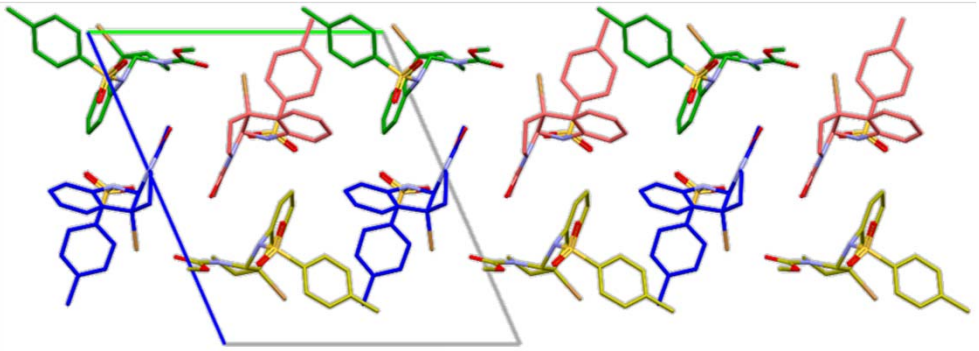
View of a layer (001)



90°



90°



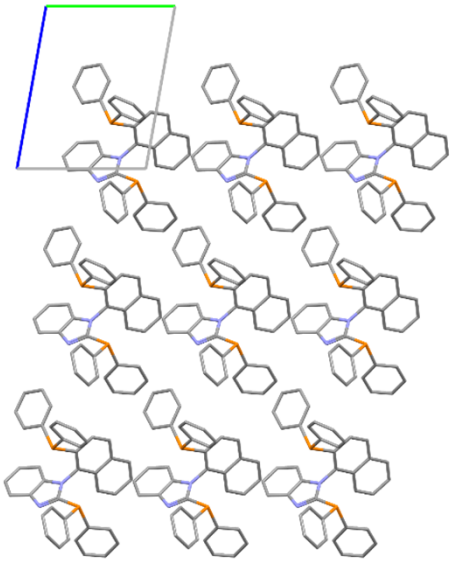
Layer (001)
*c*211, *z*=8, *z'*=2
axes [100], [$\bar{1}$20]

Other pairs of molecules (*eg*, #1&2, #1&3) are related by twofold axes that are more approximate, but the directions of those axes are not simple

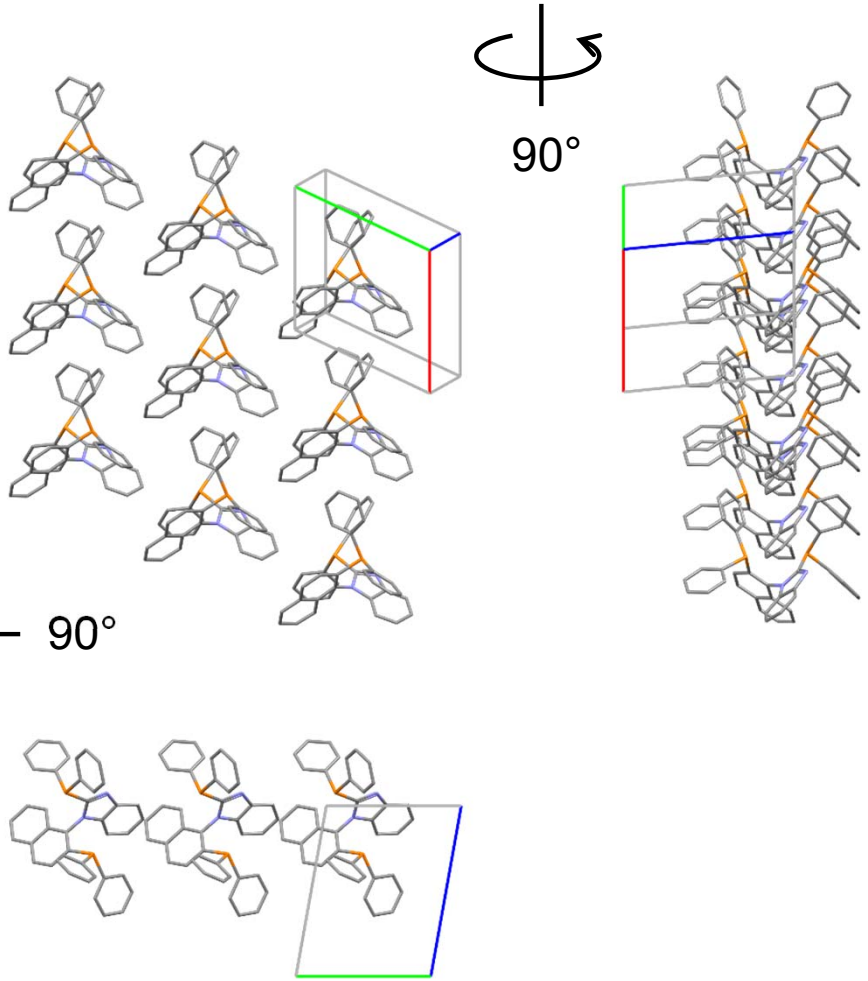
2&2$_1$, 2-D mimic

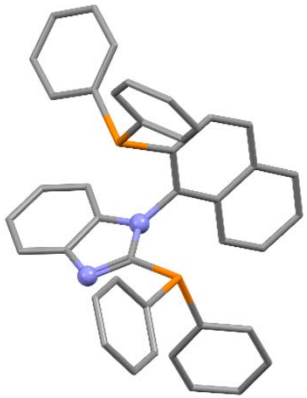
CUWBIG
(*P*1, *Z*=1)

View along **a**



Layer (001)
*c*211, *Z*=2, *Z'*=½
axes [100], [120]





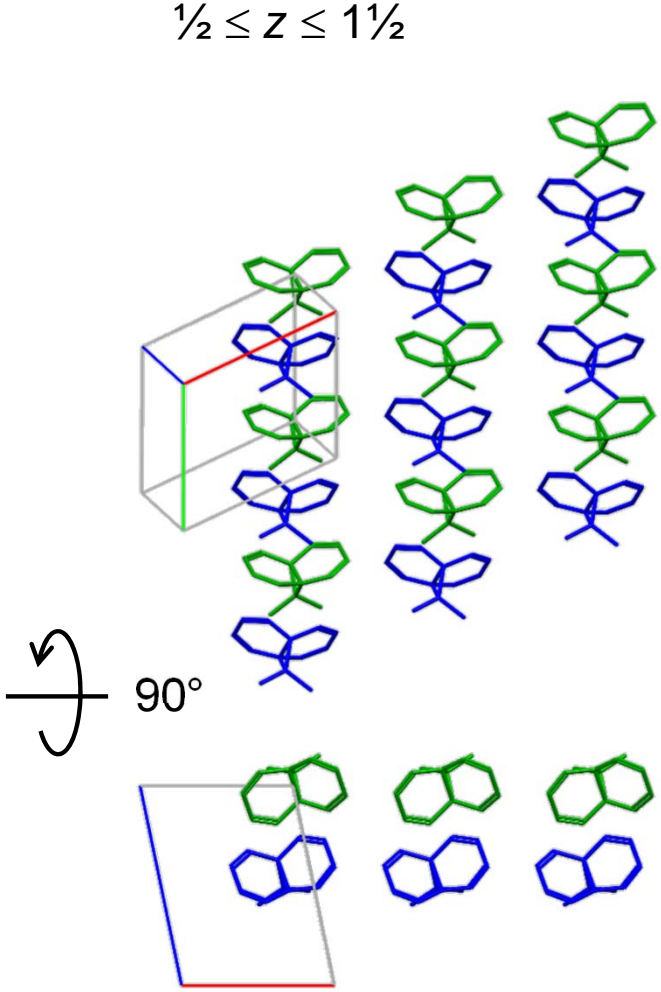
The molecule has approximate twofold symmetry if the difference between the linked C_6 and C_3N_2 rings is ignored

2&2$_1$, 2-D (achiral molecule)

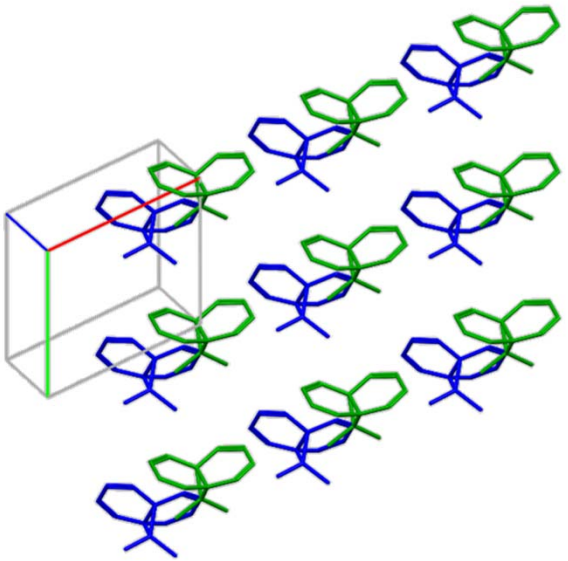
DMTCUN10
(*P*1, *Z*=2)

View along **c*** of layer (001)

½ ≤ *z* ≤ 1½

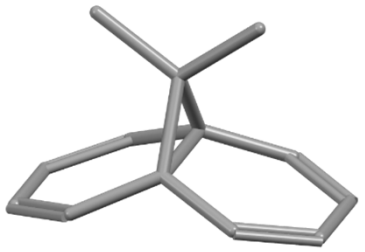


0 ≤ *z* ≤ 1



Layer (001)
*c*211, *Z*=4, *Z'*=1
axes [010], [210]

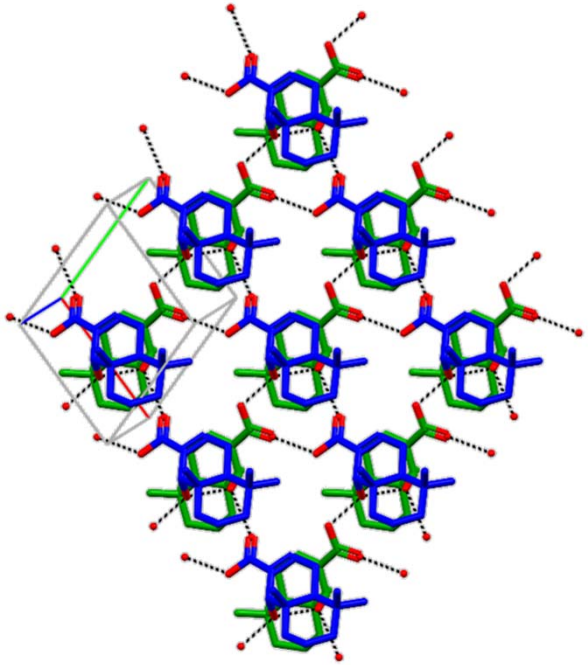
The achiral molecule very nearly has symmetry *2mm*.
Packing is nearly the same as in MMANCN, where the molecule has only approximate mirror symmetry.



2&2$_1$, 2-D showing deviations from approximate 3-D symmetry

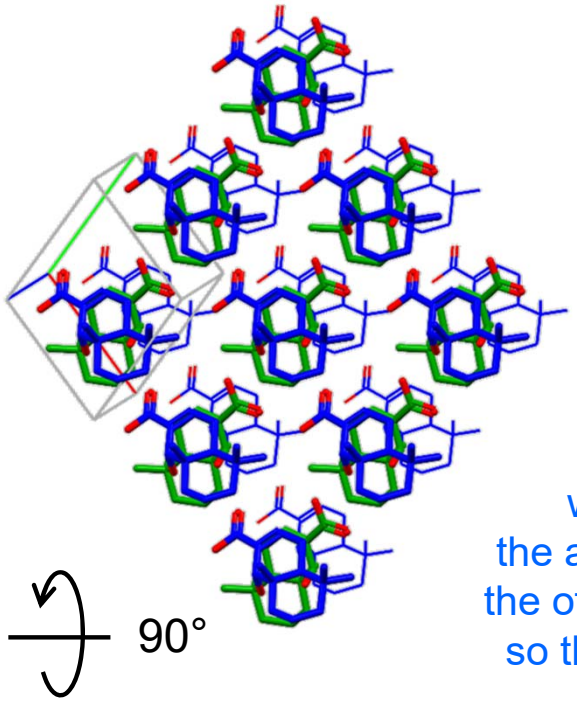
FUZTIE
(*P*1, *Z*=2)

View of a layer (001)

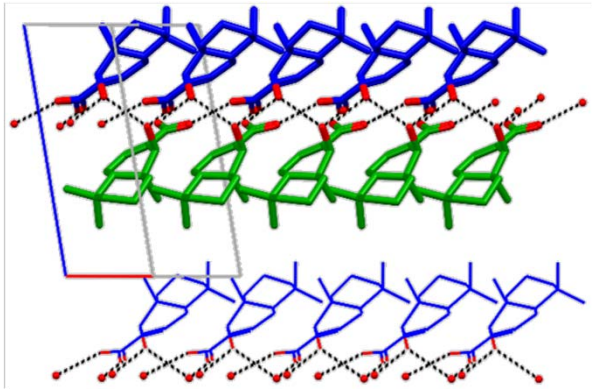


Layer (001)
*c*211, *z*=4, *z'*=1
axes [1$\bar{1}$0], [110]

View of 1.5 layers (001)



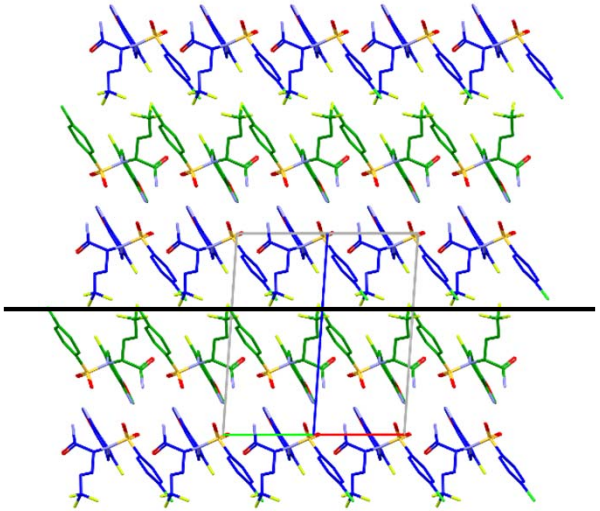
*If C*2, *z*=4, *z'*=1
with axes [110], [1$\bar{1}$0], [001]
the angles are 95.9, 99.6, 90.1° but
the offset of the next layer is obvious
so that *c*211 is a better description



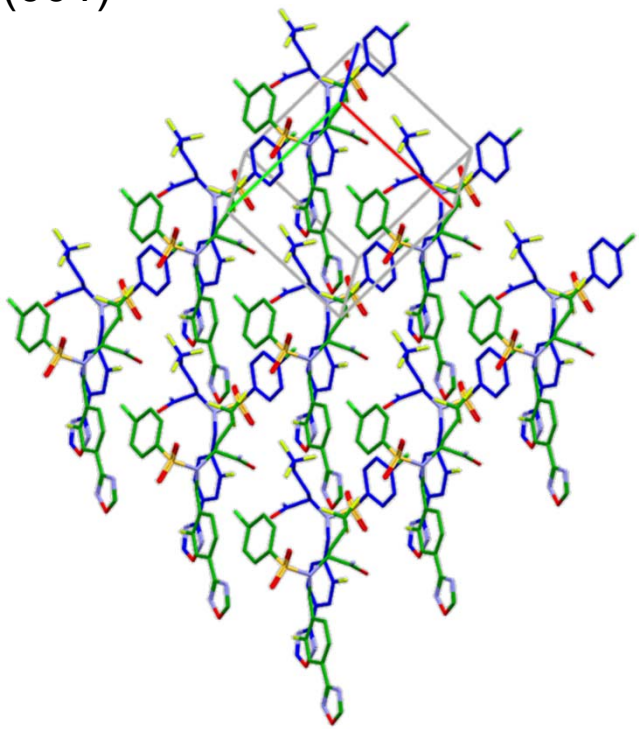
2&2$_1$, 2-D

GESYUA
(*P*1, *Z*=2)

View along [110]

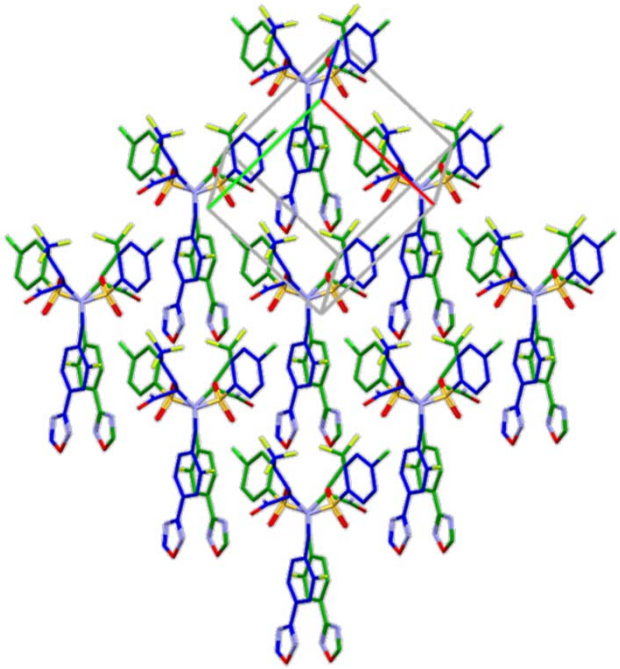


(001)



$0 \le z \le 1$

Layer (001)
*c*211, *z*=4, *z'*=1
axes [110], [1$\bar{1}$0]

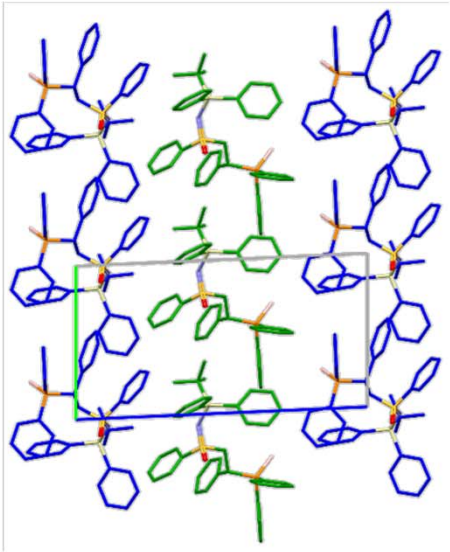


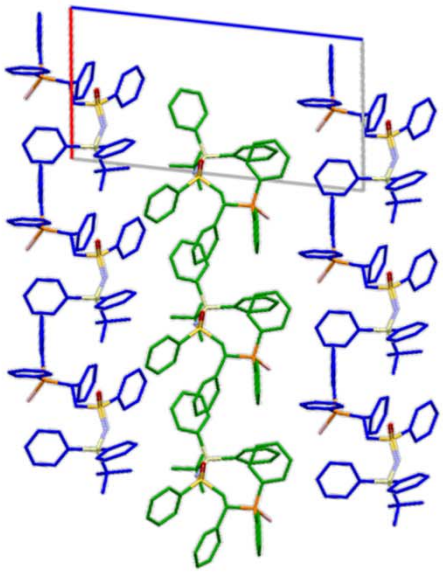
$\frac{1}{2} \le z \le 1\frac{1}{2}$

2&2$_1$, 2-D

GUWJIS
(*P*1, *Z*=2)

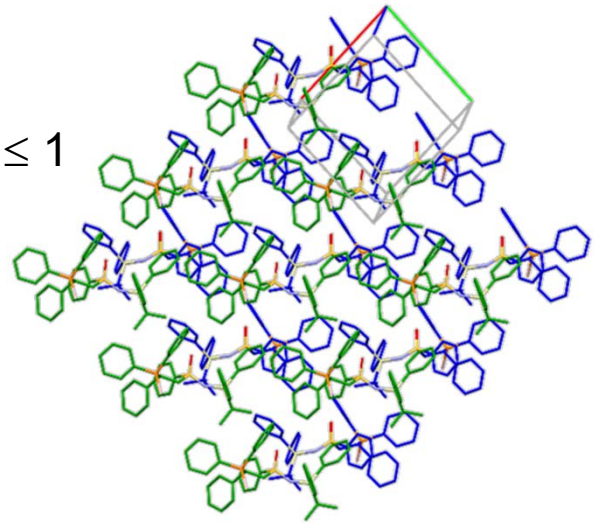
Views along **a** and **b**





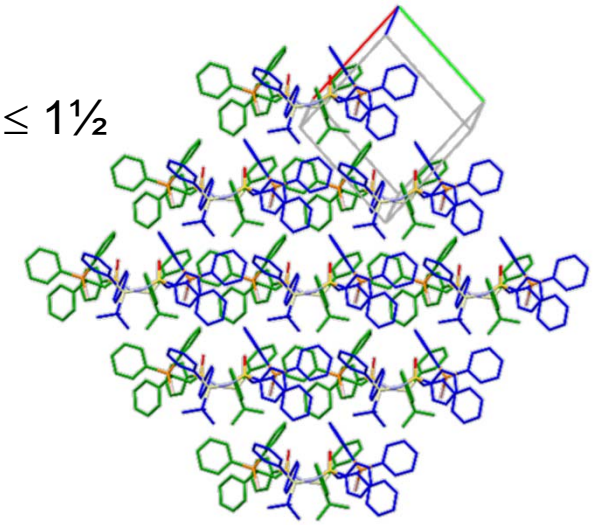
Layers (001)

$0 \le z \le 1$



The molecules are closer together for $0 \le z \le 1$ but the symmetry is much more approximate

$\frac{1}{2} \le z \le 1\frac{1}{2}$

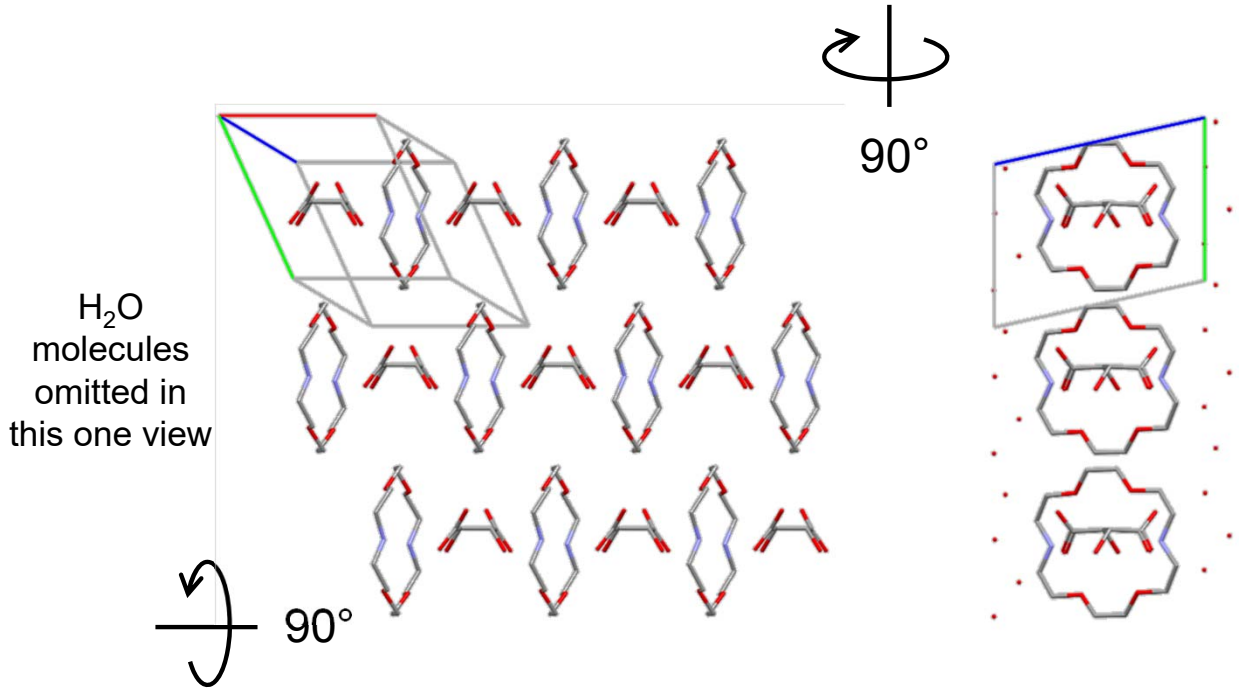


Layer (001)
*c*211, *z*=4, *z'*=1
axes [110], [1$\bar{1}$0]

2&2$_1$, 2-D

LOFJOF
(*P*1, *Z*=1)

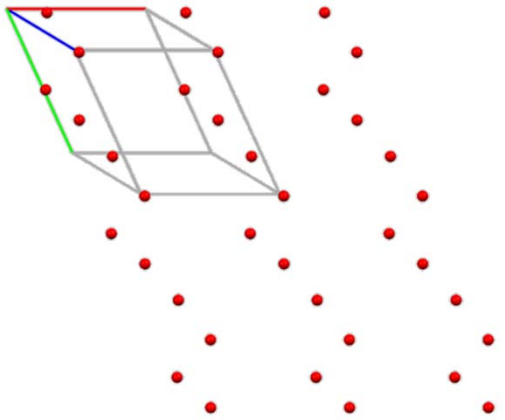
View of a layer (001)



H_2O molecules omitted in this one view

Layer (001)
*c*211, *z*=2, *z*'= ½
axes [100], [$\bar{1}$20]

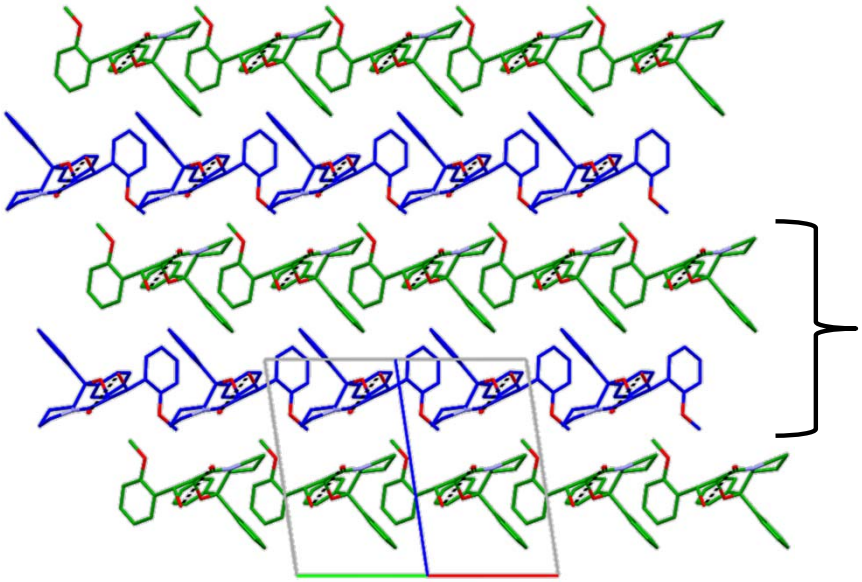
The H_2O molecules of the tetrahydrate form layers that have no symmetry other than translation



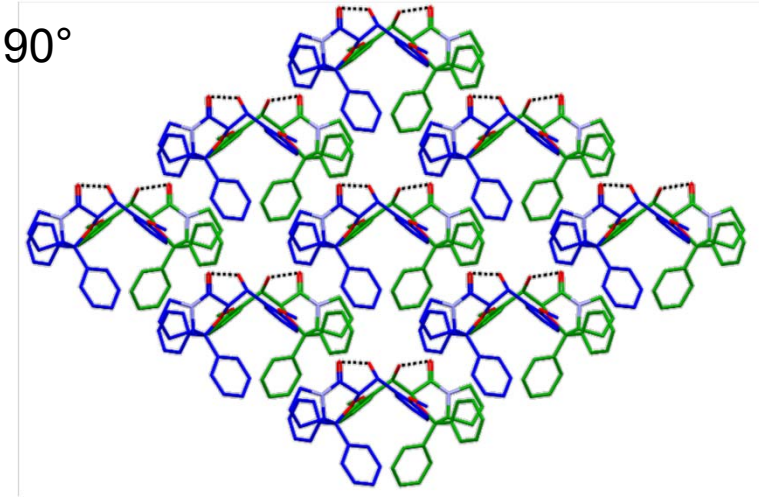
2&2$_1$, 2-D

LUSMAN
(*P*1, *Z*=2)

View along [110]



90°



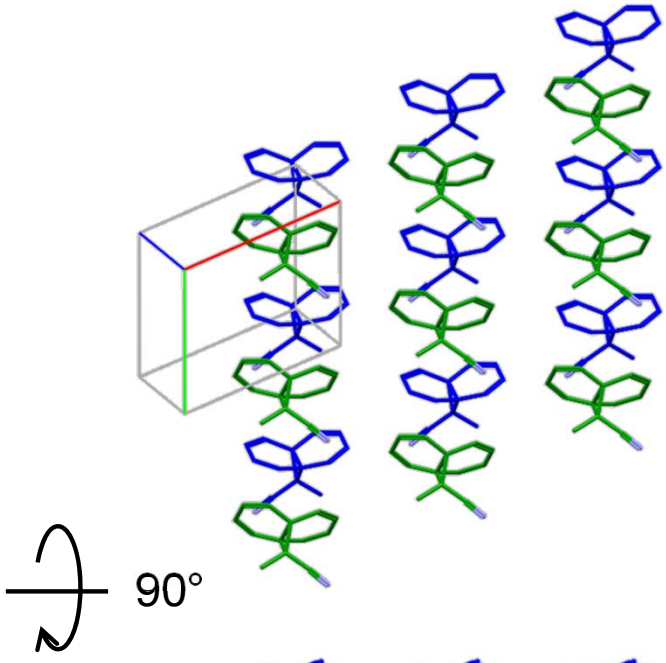
Layer (001)
*c*211, *z*=4, *z'*=1
axes [110], [1$\bar{1}$0]

2&2$_1$, 2-D (achiral molecule)

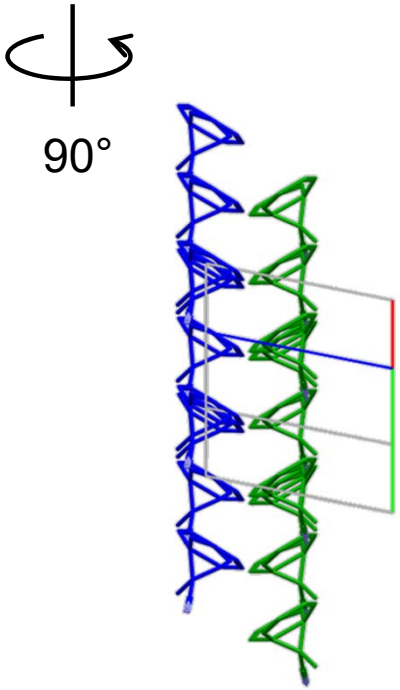
MMANCN
(*P*1, *Z*=2)

View along **c*** of layer (001)

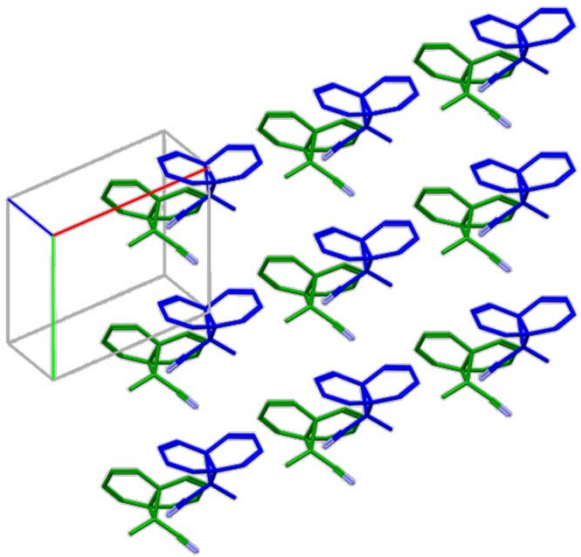
½ ≤ *z* ≤ 1½



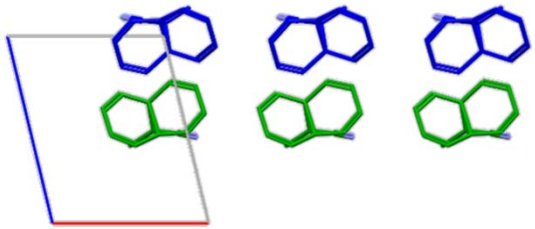
90°



0 ≤ *z* ≤ 1

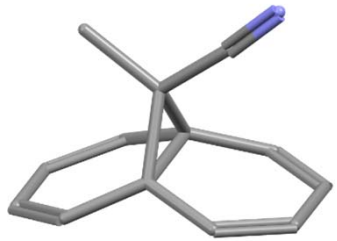


90°



Layer (001)
*c*211, *Z*=4, *Z'*=1
axes [010], [210]

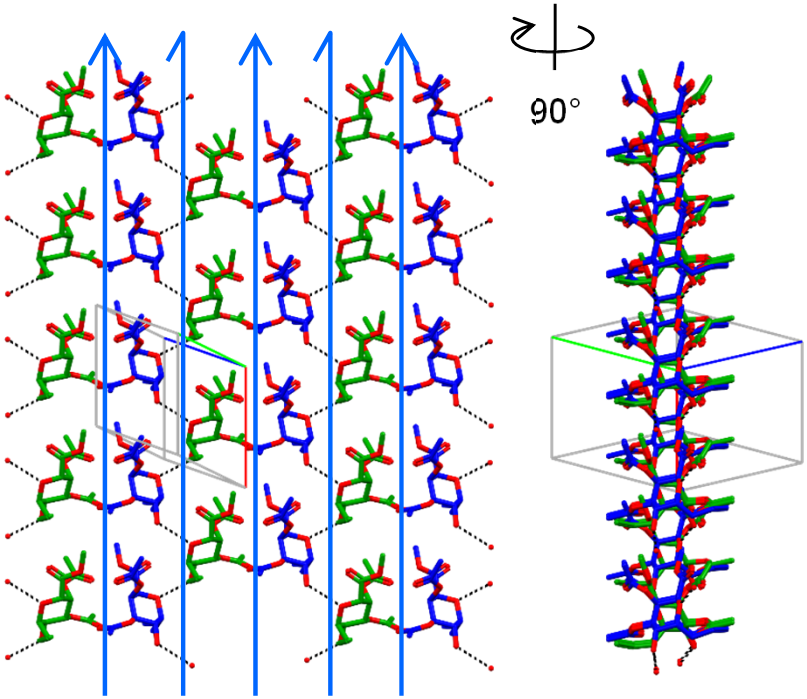
The achiral molecule very nearly has symmetry *m*. Packing is nearly the same as in DMTCUN10, in which the molecule nearly has symmetry *2mm*



2&2$_1$, 2-D (not 3-D even though there is a cell with twofold axes and α, γ = 91.0, 90.5°)

PANFOA
(*P*1, *Z*=2)

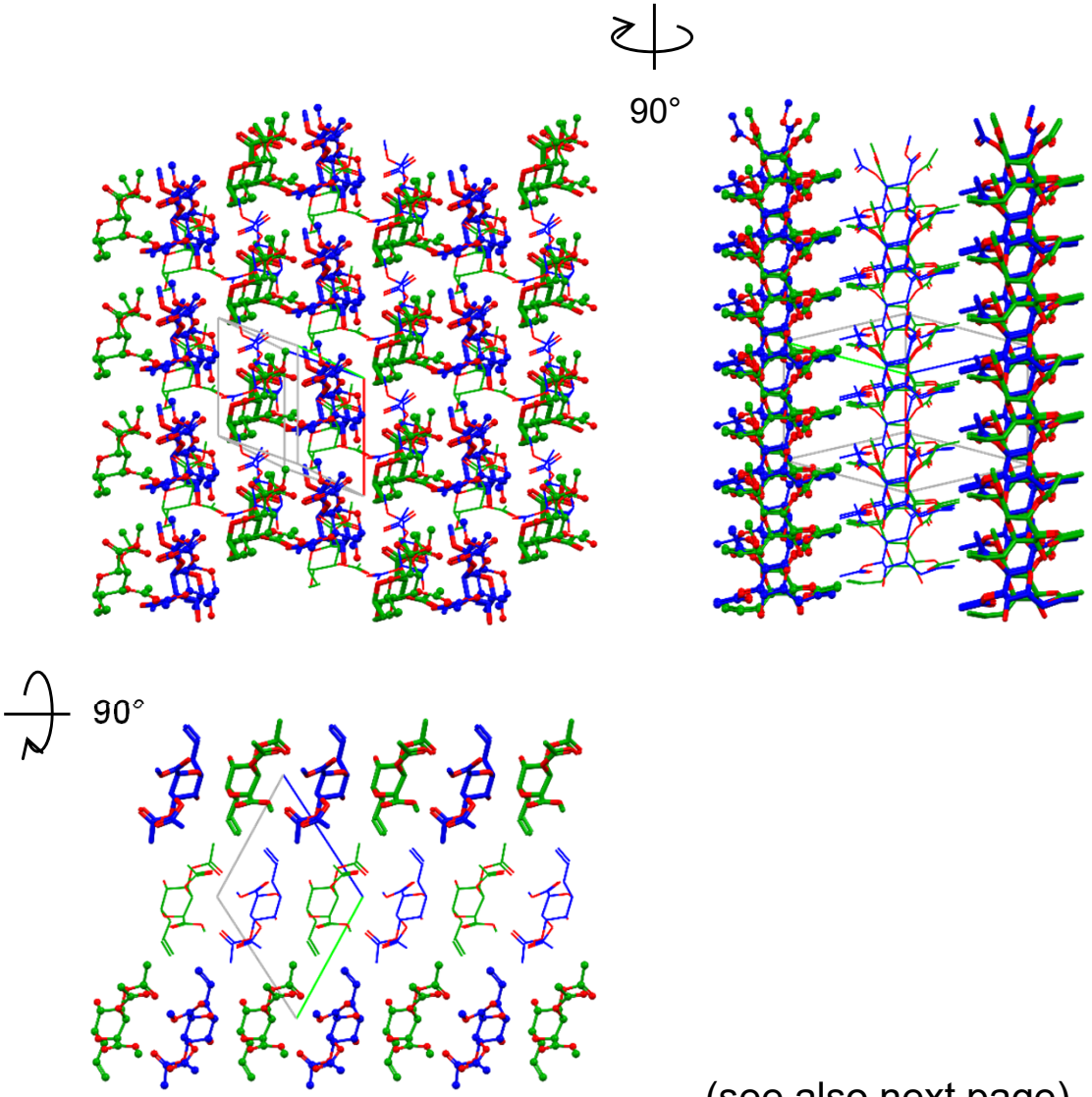
Layer (01$\bar{1}$)



(H-bonds shown in this view only)

Layer (01$\bar{1}$), *c*211, *z'*=1
axes [100], [122];
angle 90.5°

Three layers (01$\bar{1}$)



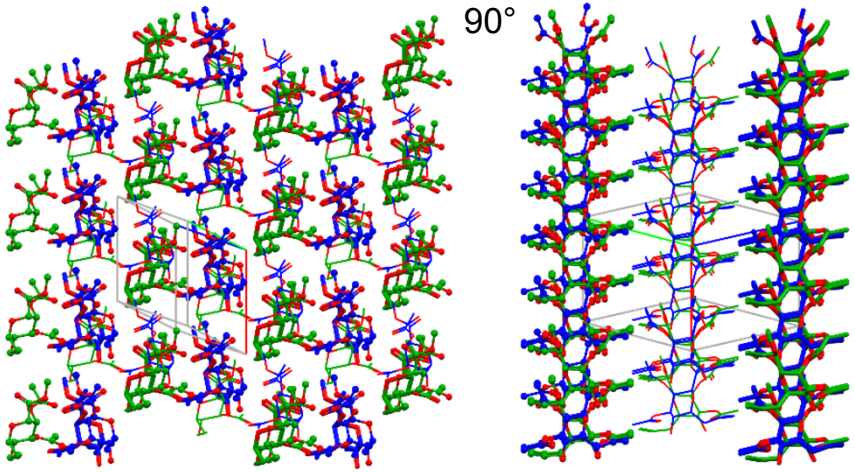
(see also next page)

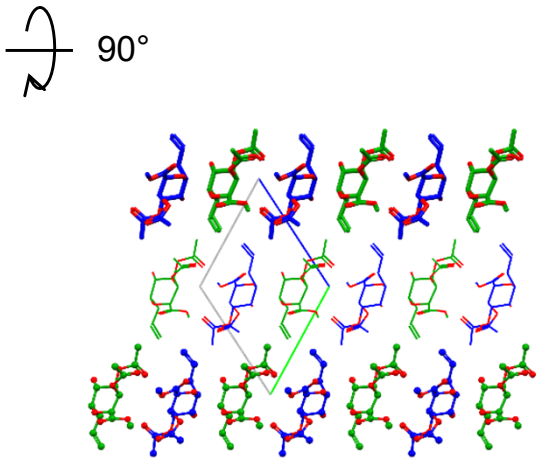
2&2$_1$, 2-D (not 3-D even though there is a cell with twofold axes and α, γ = 91.0, 90.5°)

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

Three layers $(01\bar{1})$

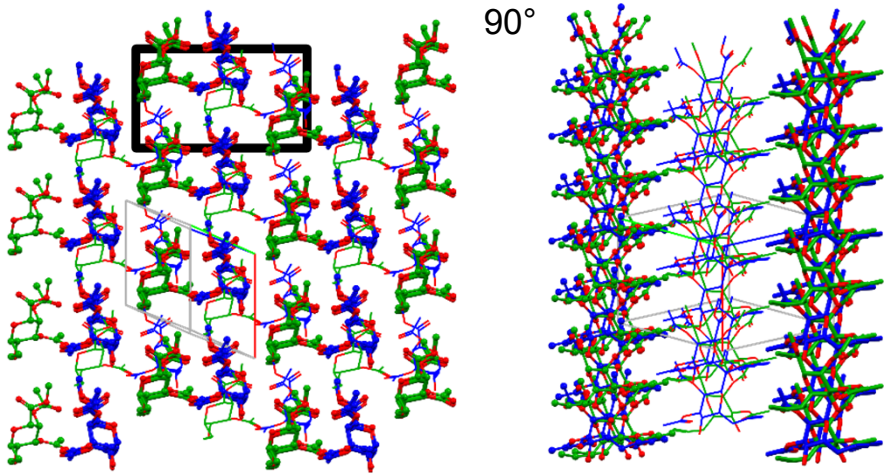
The 1st and 3rd layers are offset

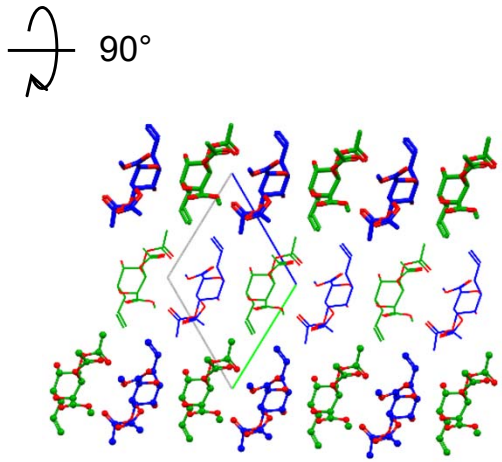




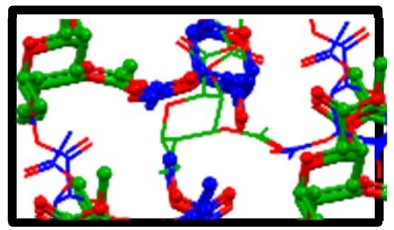
Three layers $(01\bar{1})$ rotated around [100] by 3°

The 1st and 3rd layers are superimposed





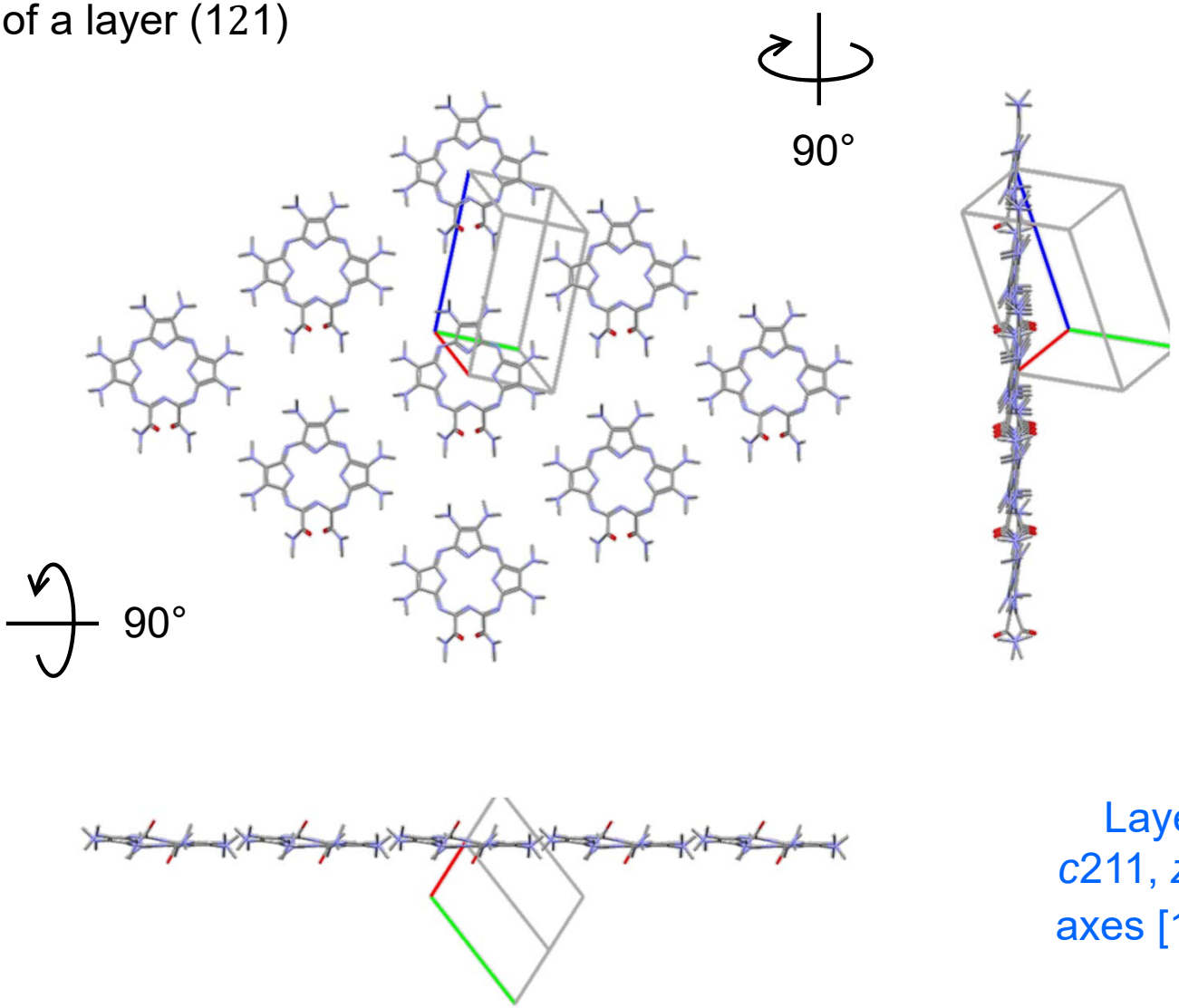
In the rotated cell adjacent layers are offset by¼ along each of the two layer axes so that 3-D $C2$ symmetry is impossible



2&2$_1$, 2-D

POGKEB
(*P*1, *Z*=1)

View of a layer (1$\bar{2}$1)



Layer (1$\bar{2}$1)
*c*211, *z*=2, *z'*= ½
axes [10$\bar{1}$], [321]

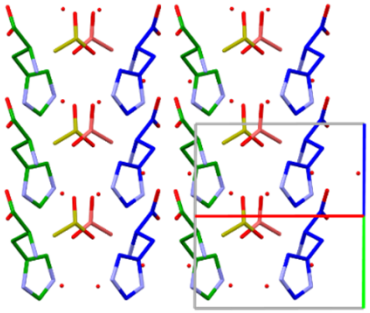
2&2$_1$, 2-D

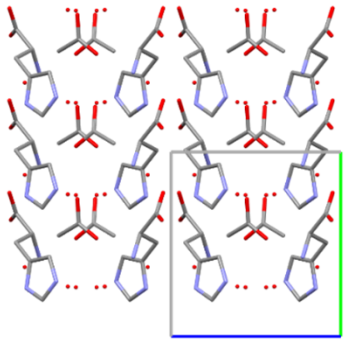
POPGUW
(*P*1, *Z*=2)
(a dihydrate)

POPGUW01 at 123 K

POPGUW at RT
(*C*2, *Z'*=1)

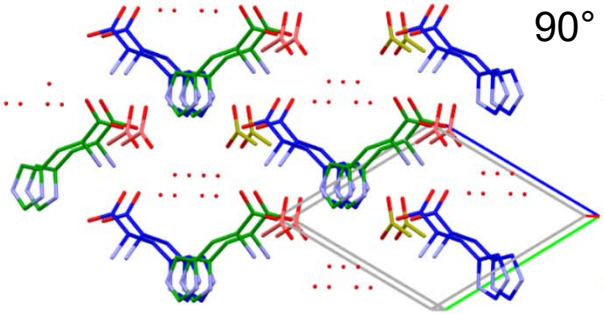
View along
[011]

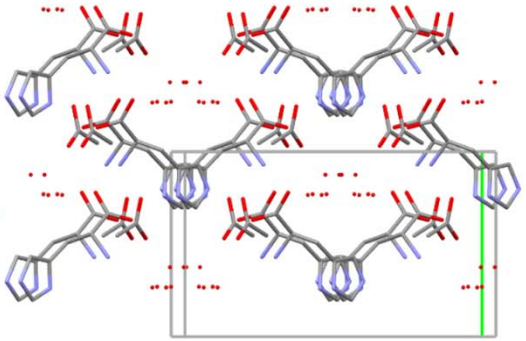




View along
[100]

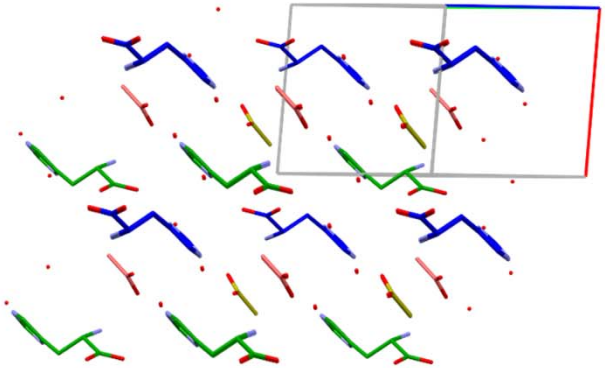
90°

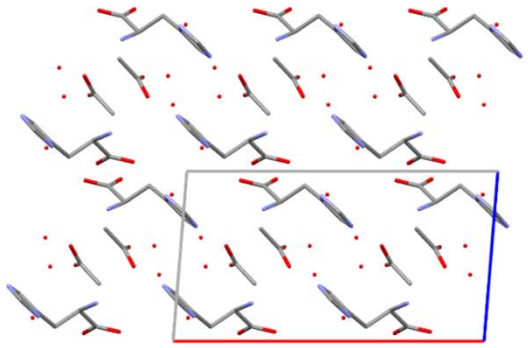




The main difference between the structures is the positions of the water molecules, one of which is disordered 76:24 in the *C*2 structure

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



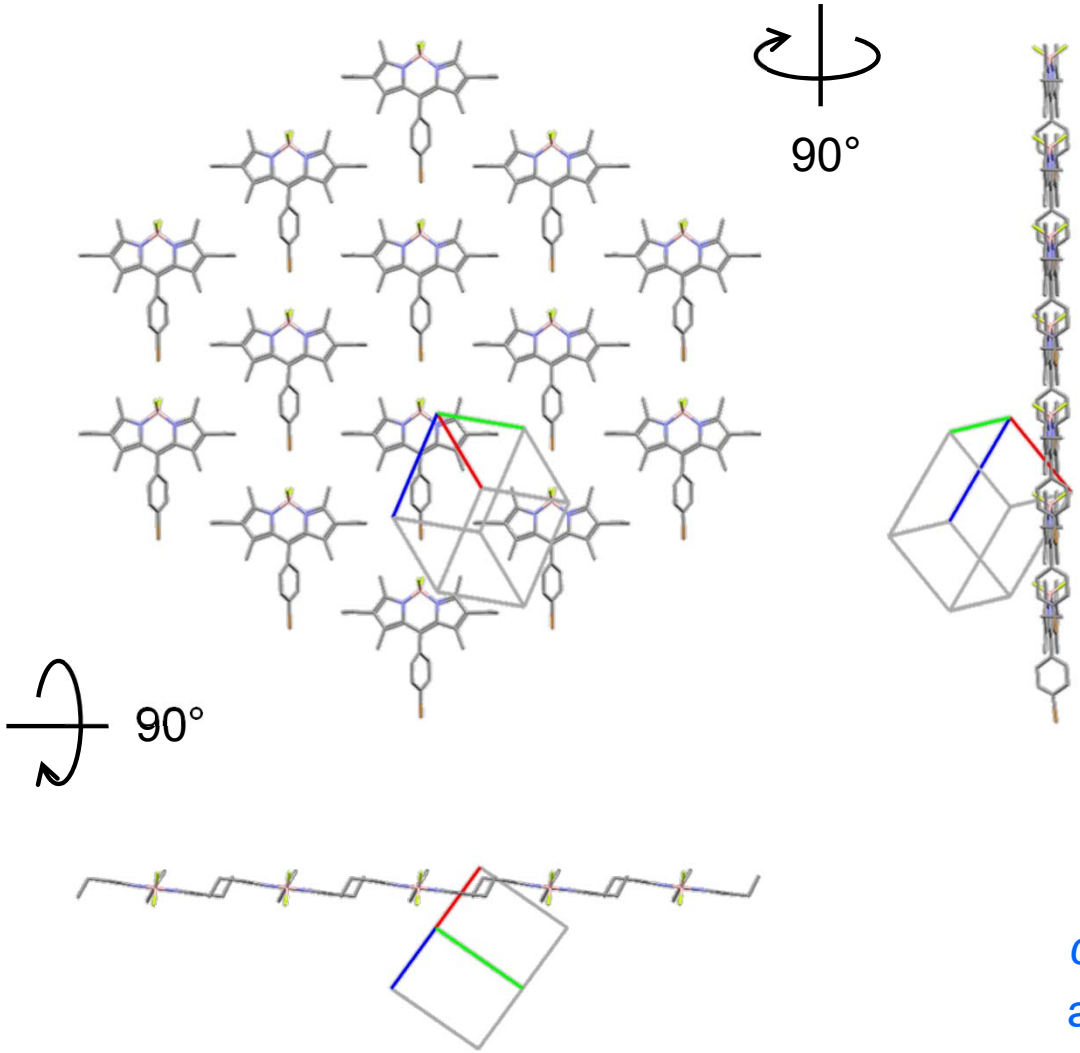


View along
[010]

2&2$_1$, 2-D

QAHSEA
(*P*1, *Z*=1)

View of a layer $(1\bar{1}\bar{1})$

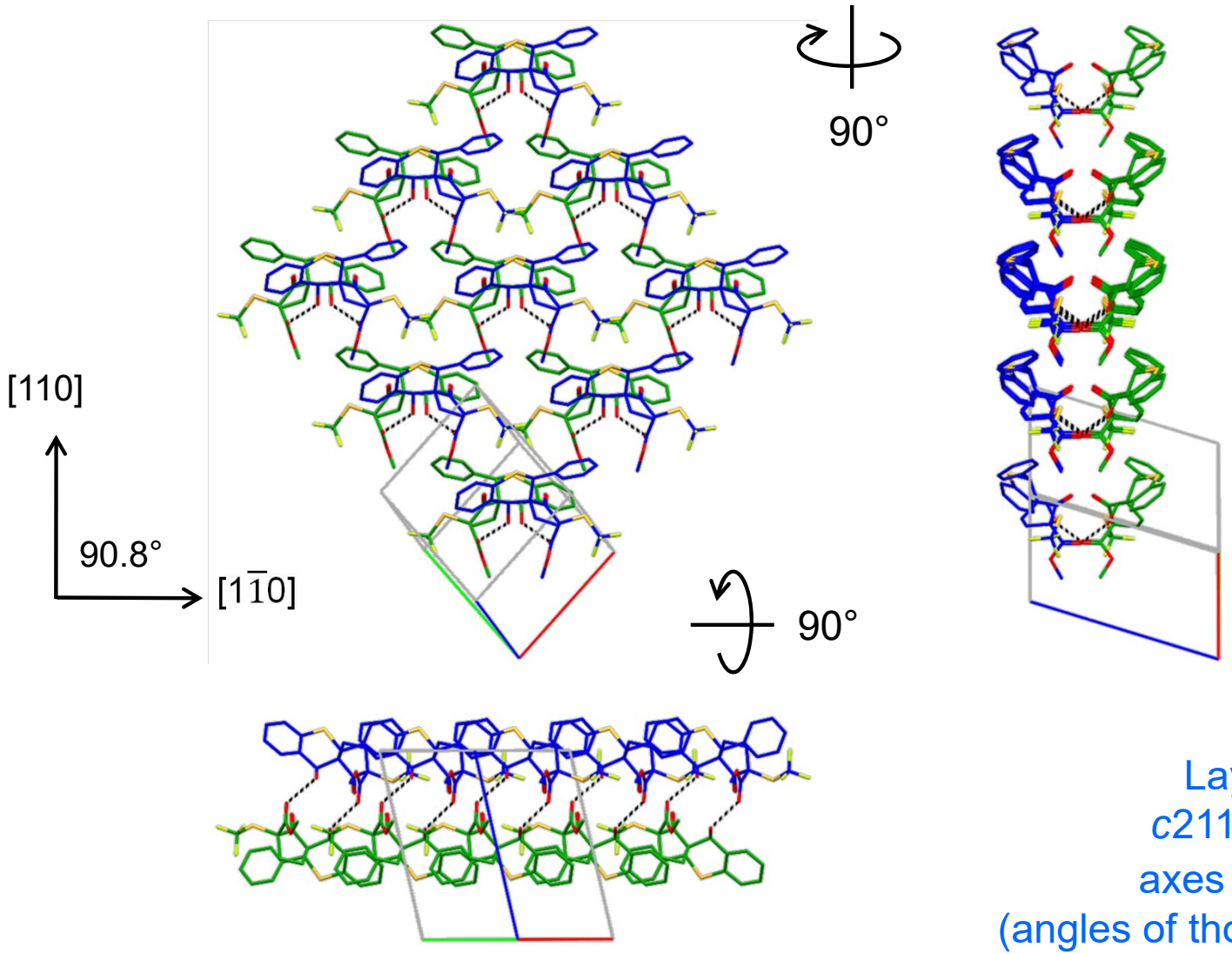


Layer $(1\bar{1}\bar{1})$
*c*211, *z*=2, *z'*= ½
axes [101], $[12\bar{1}]$

2&2$_1$, 2-D

QAXCUQ
(*P*1, *Z*=2)

View of a layer (001)

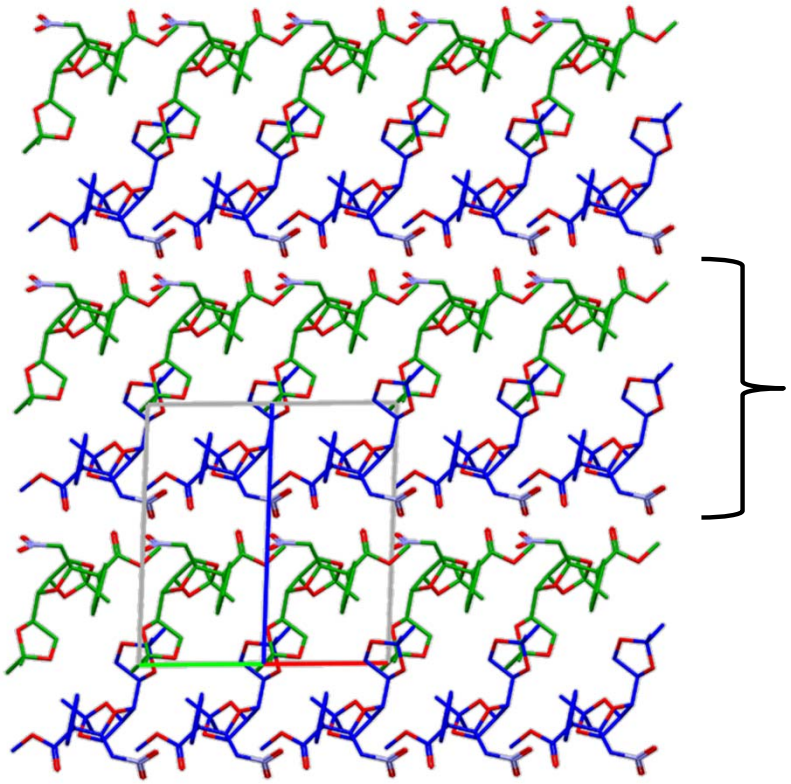


Layer (001)
*c*211, *z*=4, *z'*=1
axes [110], [1$\bar{1}$0]
(angles of those two axes with **c** are 106.6, 77.6°)

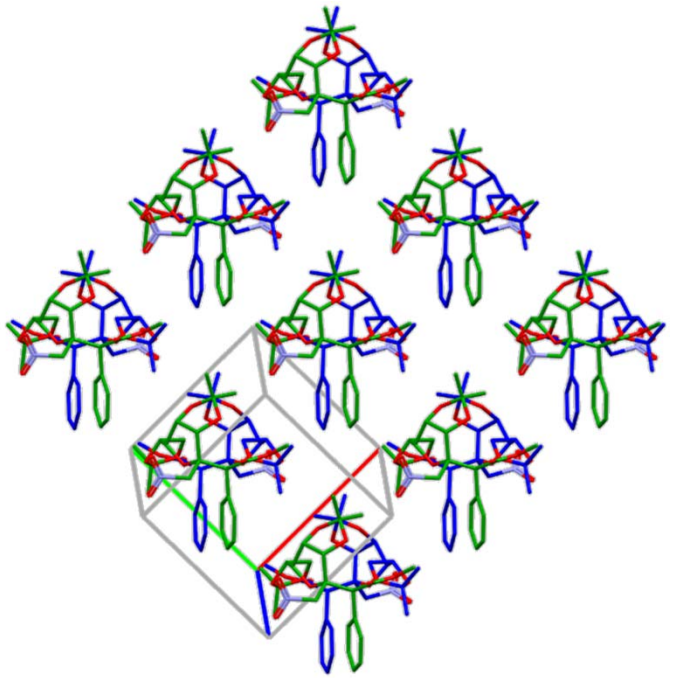
2&2$_1$, 2-D

ROJZIB
(*P*1, *Z*=2)

View along [110]



90°



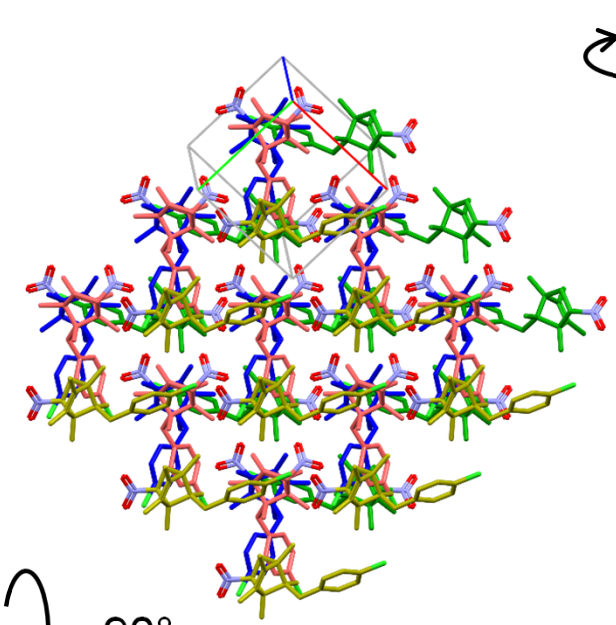
½ ≤ *z* ≤ 1½

Layer (001)
*c*211, *z*=4, *z'*=1
axes [110], [1$\bar{1}$0]

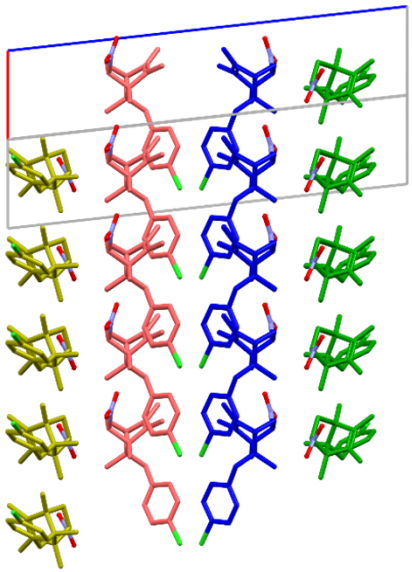
2&2$_1$, 2-D

SEMBAP
(*P*1, *Z*=4)

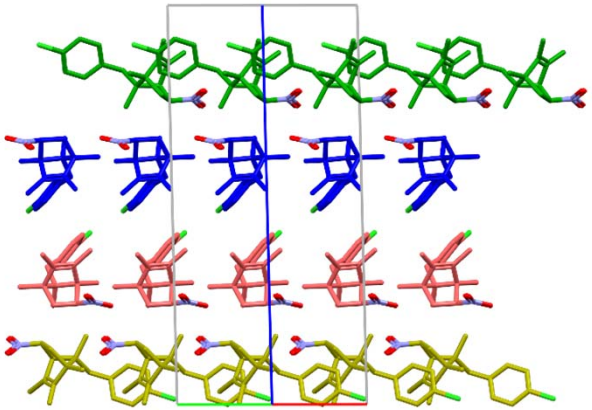
View of layer (001),
0<*z*<1



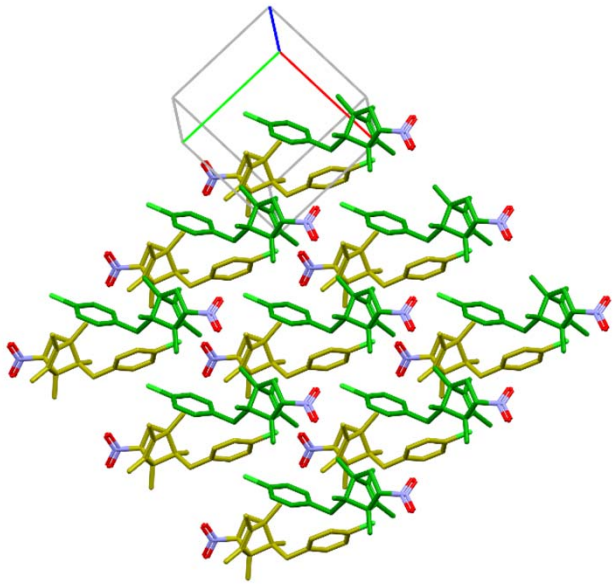
90°



90°



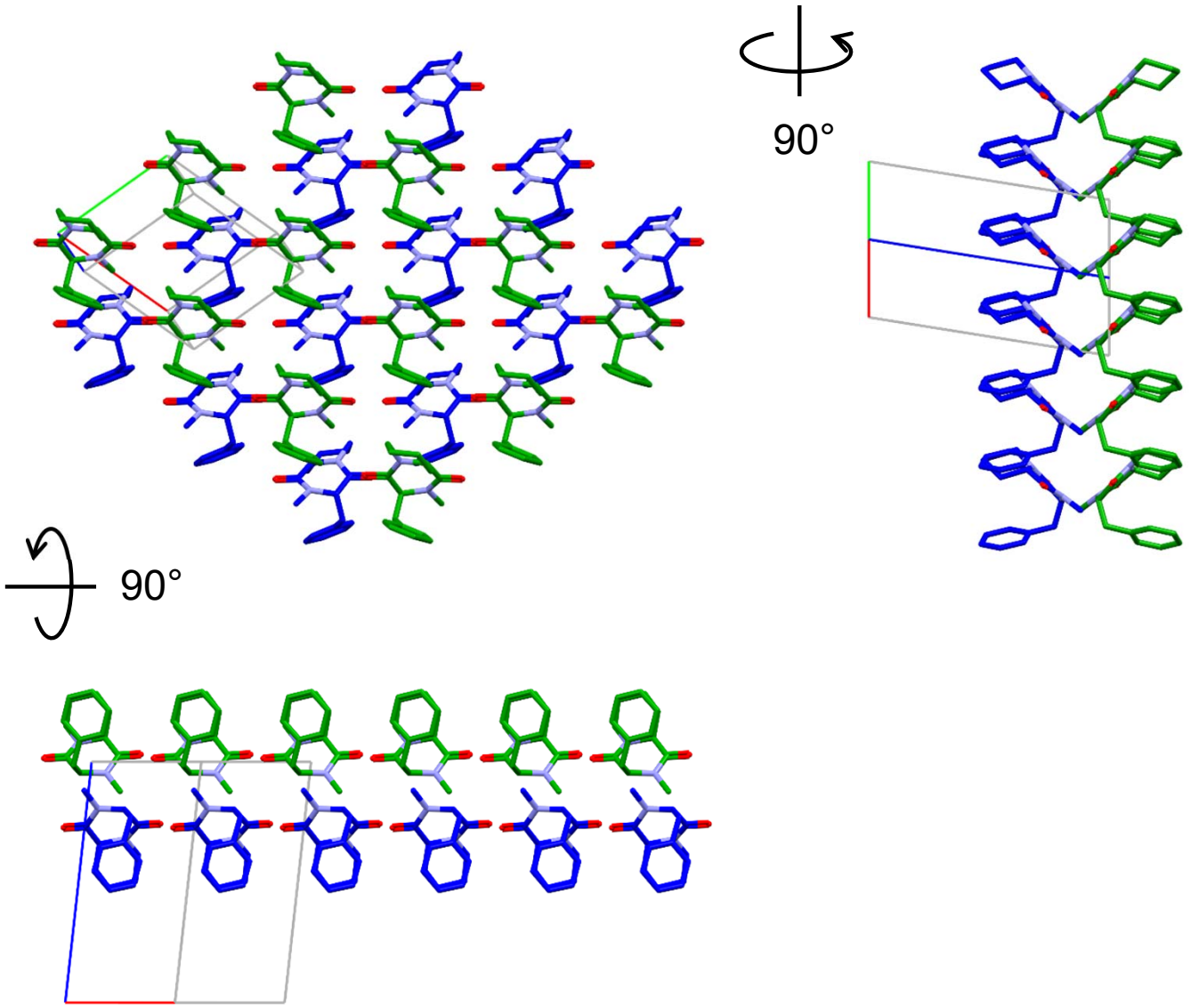
Layer (001),
-0.2<*z*<0.2
showing effects of
the layer offset



2&2$_1$, 2-D

UKOBIG
(*P*1, *Z*=2)

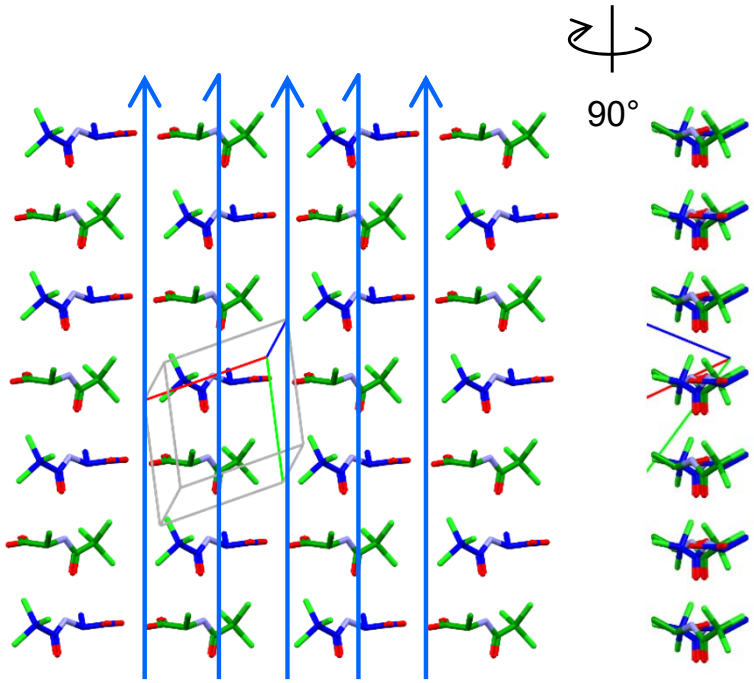
View of layer (001)



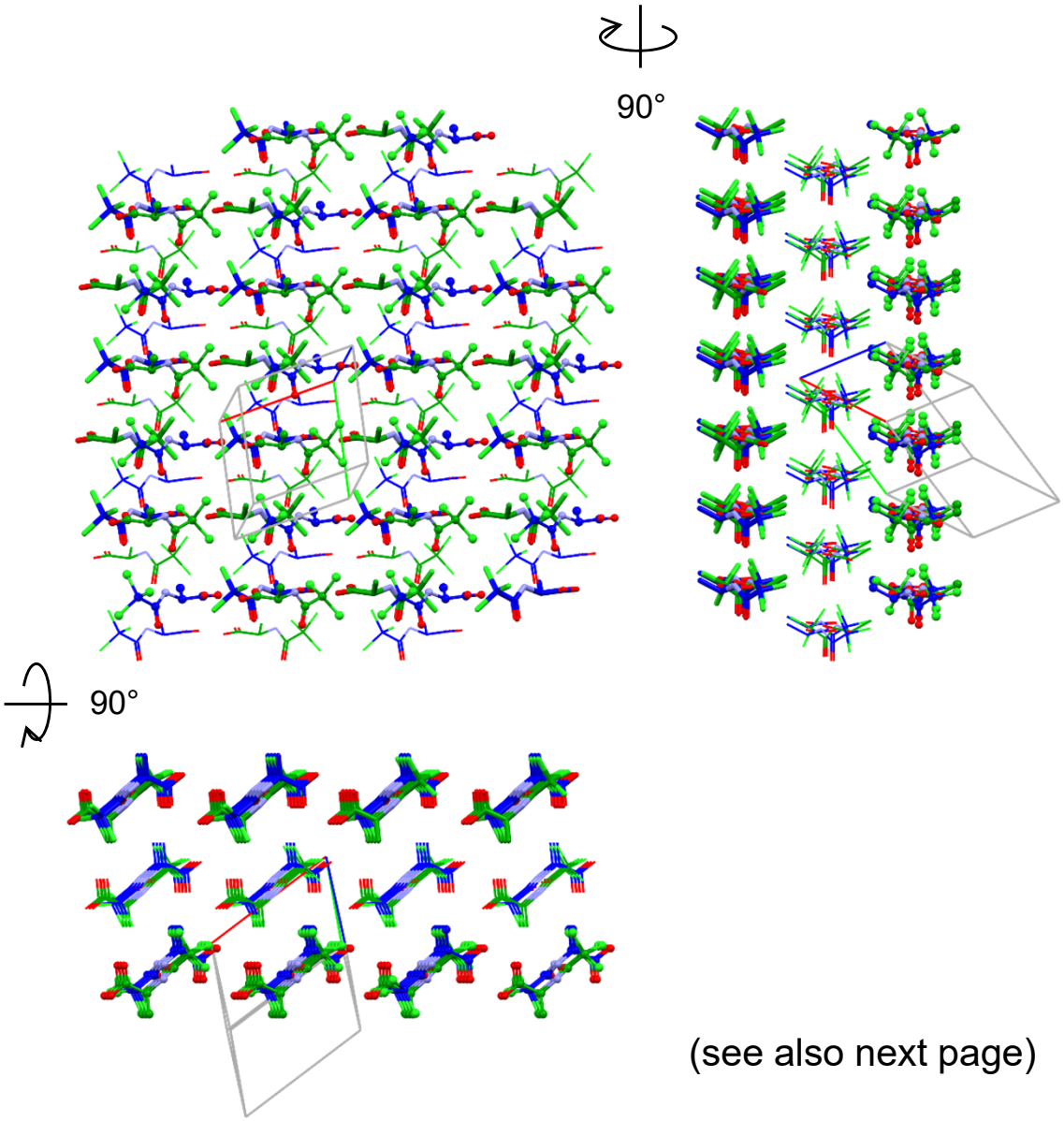
2&2$_1$, 2-D (not 3-D even though there is a cell with twofold axes and α, γ = 87.8, 91.4°)

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

Layer (111)



Three layers (111)



Layer (111), *c*211, *z'*=1
axes [01$\bar{1}$], [2$\bar{1}\bar{1}$];
angle 88.6°

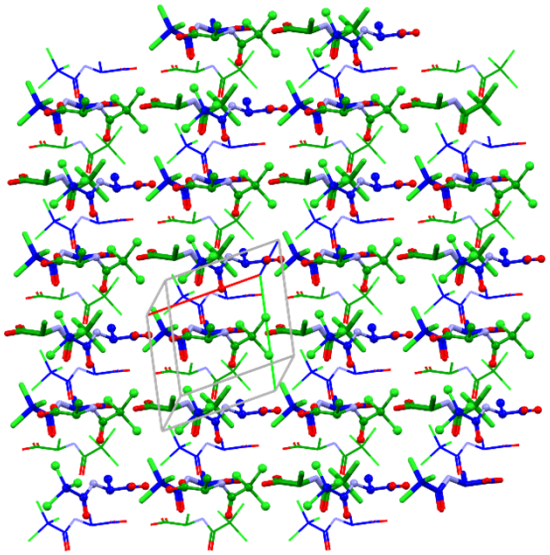
(see also next page)

2&2$_1$, 2-D (not 3-D even though there is a cell with twofold axes and α, γ = 87.8, 91.4°)

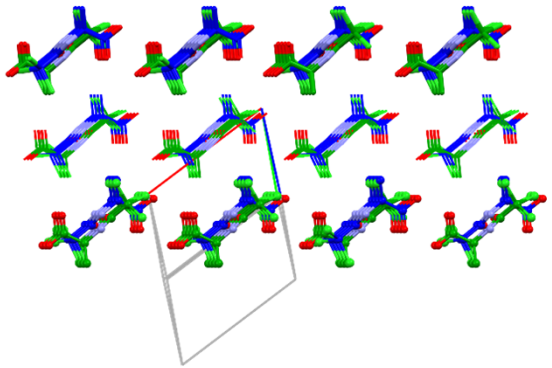
ZIYNAW, con't
(*P*1, *Z*=2)

Three layers (111)

The 1st and 3rd layers are offset

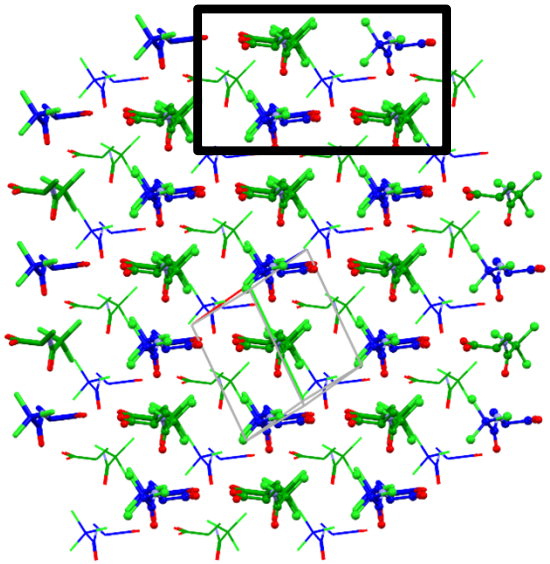


90°

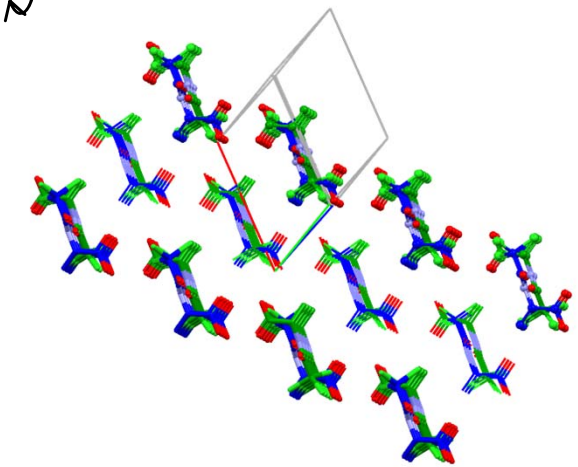


Three layers (111)
rotated around [01$\bar{1}$] by 29°

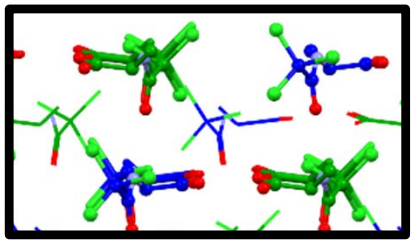
The 1st and 3rd layers are superimposed



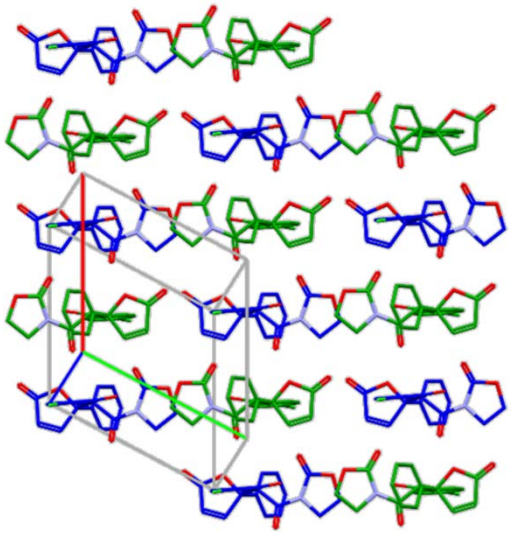
90°



In the rotated cell adjacent layers are offset by¼ along each of the two layer axes so that 3-D *C*2 symmetry is impossible

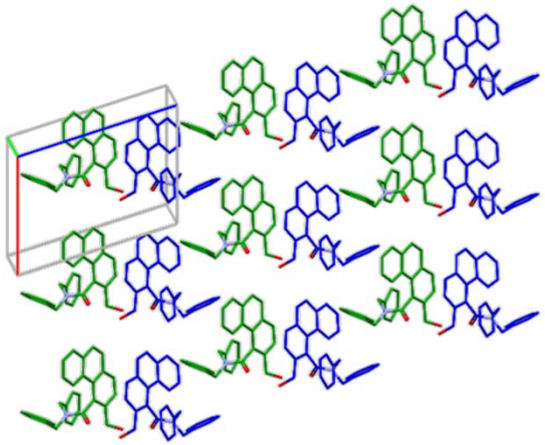


Additional examples of *c*211 (the approximate twofold axes are all vertical)



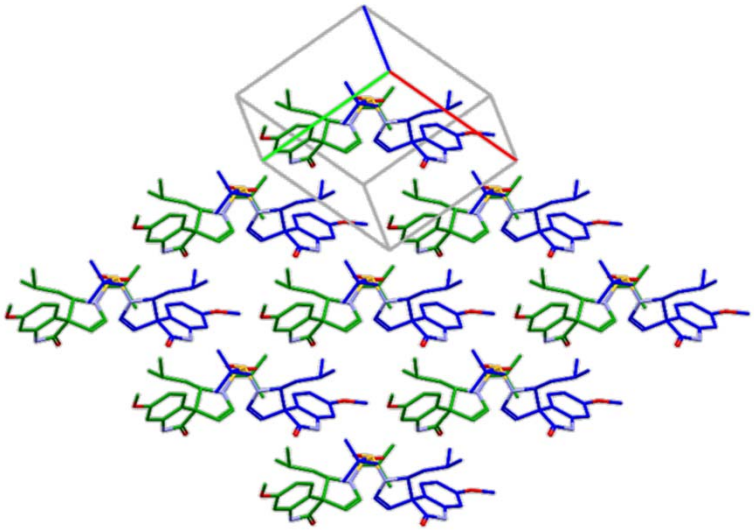
CANBEB

Layer (001)
axes [100], [120]



ITAVOQ

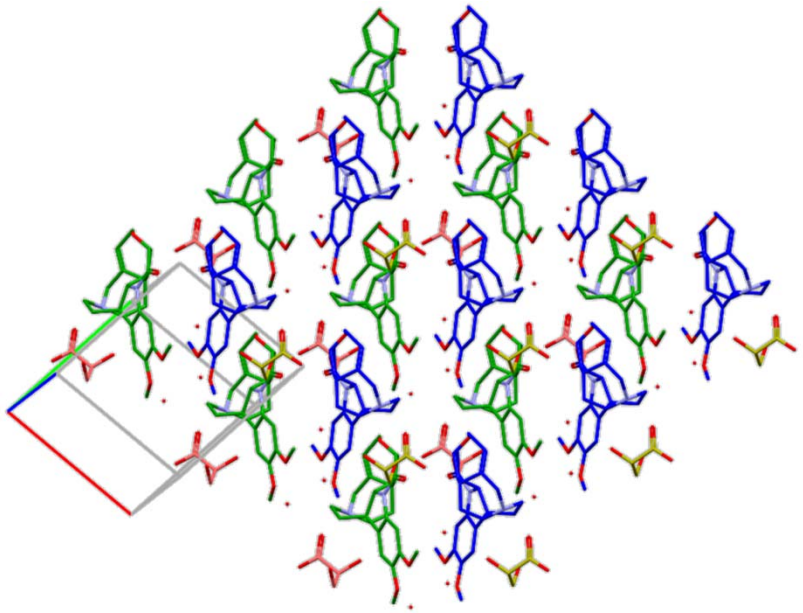
Layer (010)
axes [100], [102]



JUVREZ

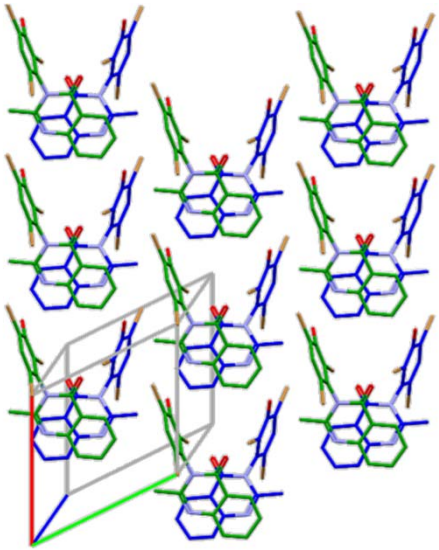
Layer (001)
axes [110], [1$\bar{1}$0]

Yet more examples of *c*211 layers (the approximate twofold axes are vertical)



QANJIZ

Layer (001)
axes [1$\bar{1}$0], [110]



TUXLIJ

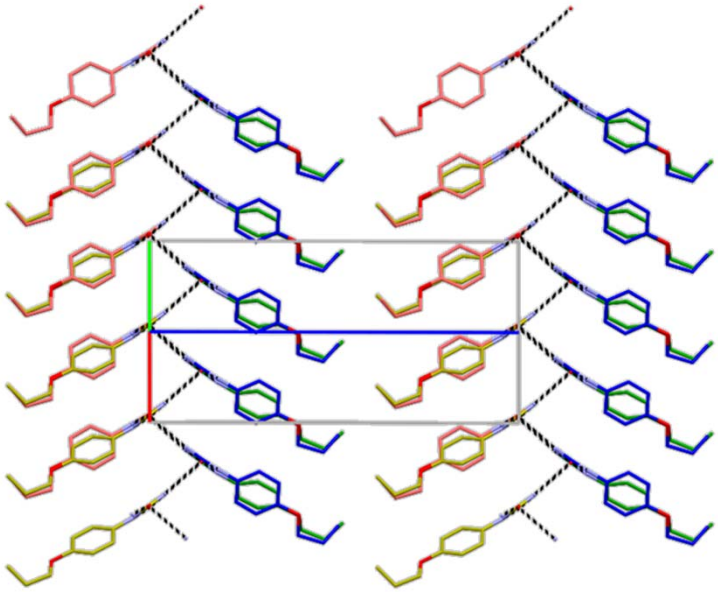
Layer (001)
axes [100], [$\bar{1}$20]

Structures that have approximate symmetry 2_1
and one (KITGEB) with approximate symmetry 3_1

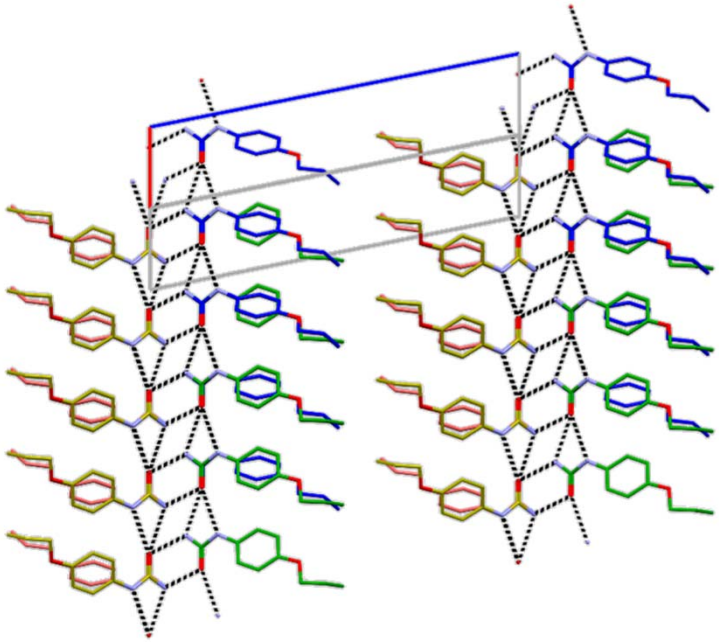
2_1, 3-D

JULTUF01
(*P*1, *Z*=4)

View along [110]



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



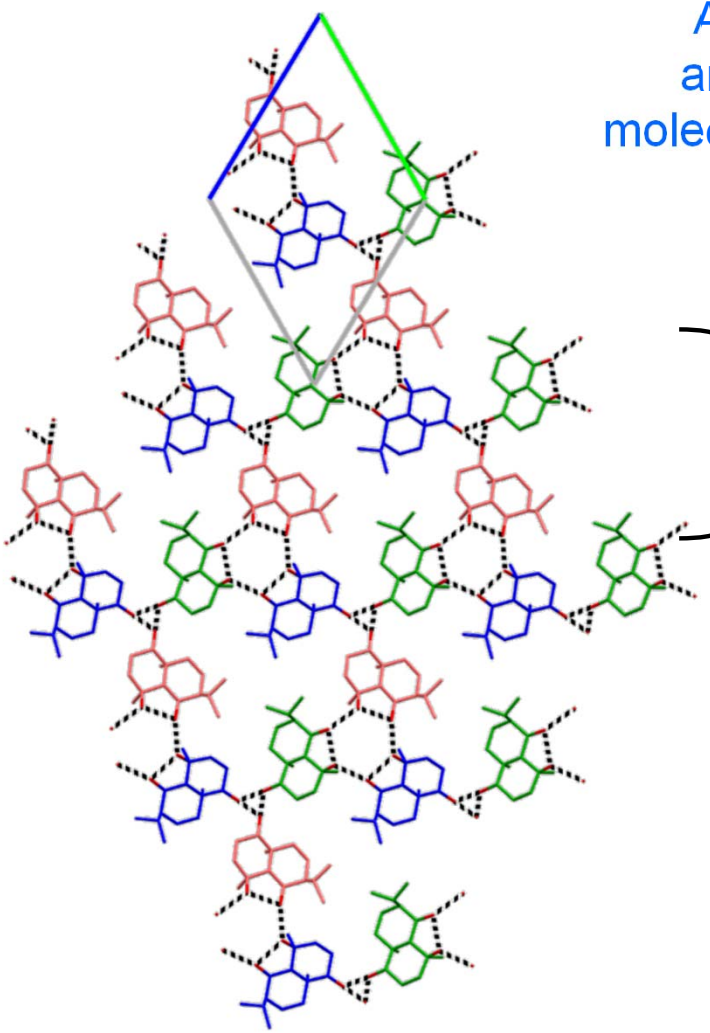
Modulated $P2_1$, *Z'*=1 structure in which the [1$\bar{1}$0] direction is unique and the approximate translations[110]/2 and [1$\bar{1}$0]/2 (=[110]/2-[010]) perturb the 2_1 symmetry; the angles of the approximate $P2_1$ cell are 90.2, 101.2, 89.9°

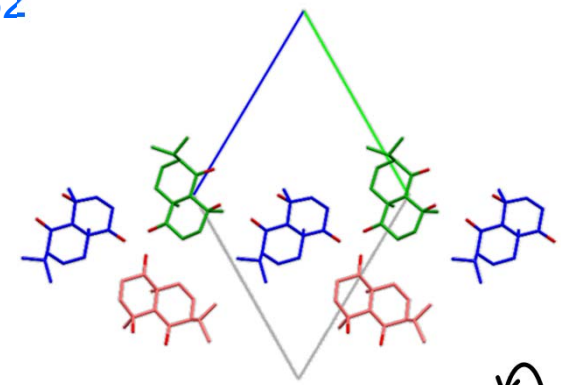
3_1, 3-D

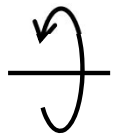
KITGEB
(*P*1, *Z*=3)

View along **a**

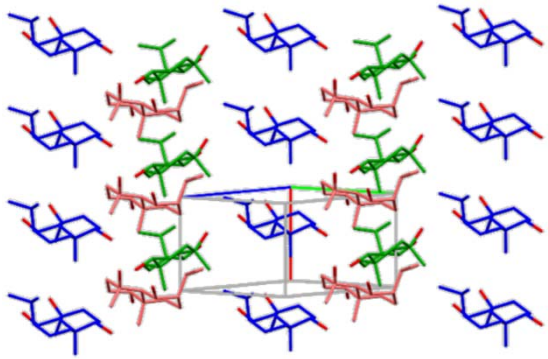
At RT, *b*=14.27, *c*=14.44 Å;
angles are 60.5, 87.3, 88.4°;
molecules are separated along **a** by
0.34, 0.34, 0.32







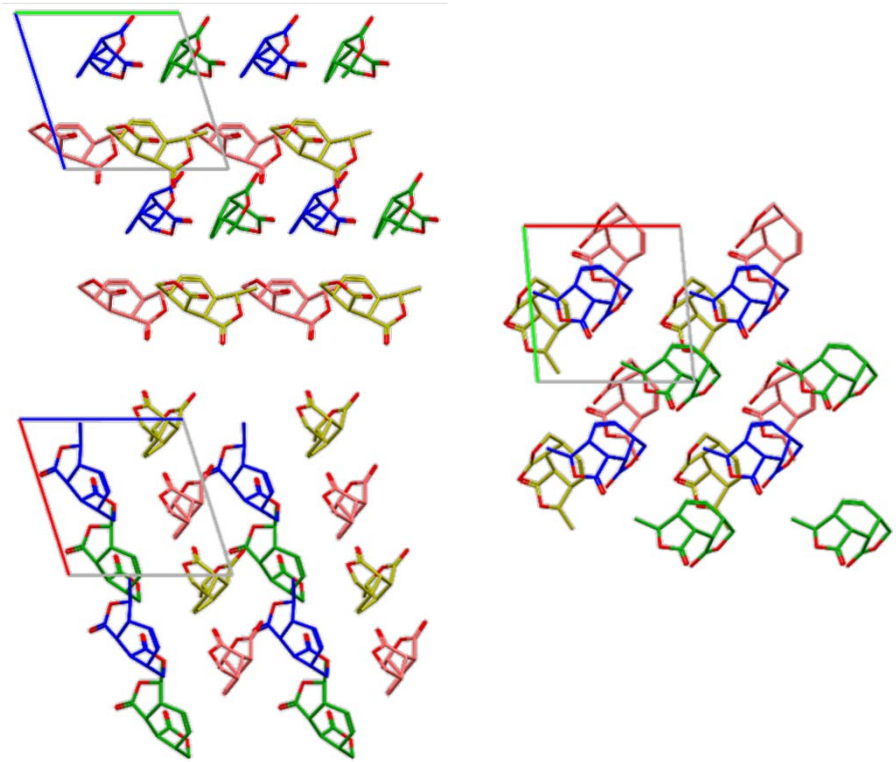
90°



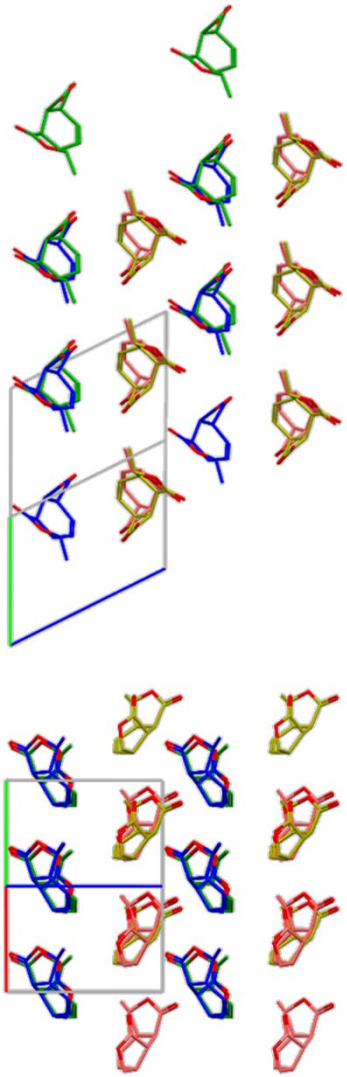
2_1, 3-D

LAQFOZ
(*P*1, *Z*=4)

Views along **a**, **b**, and **c**



Views along [1$\bar{1}$0] and [110]

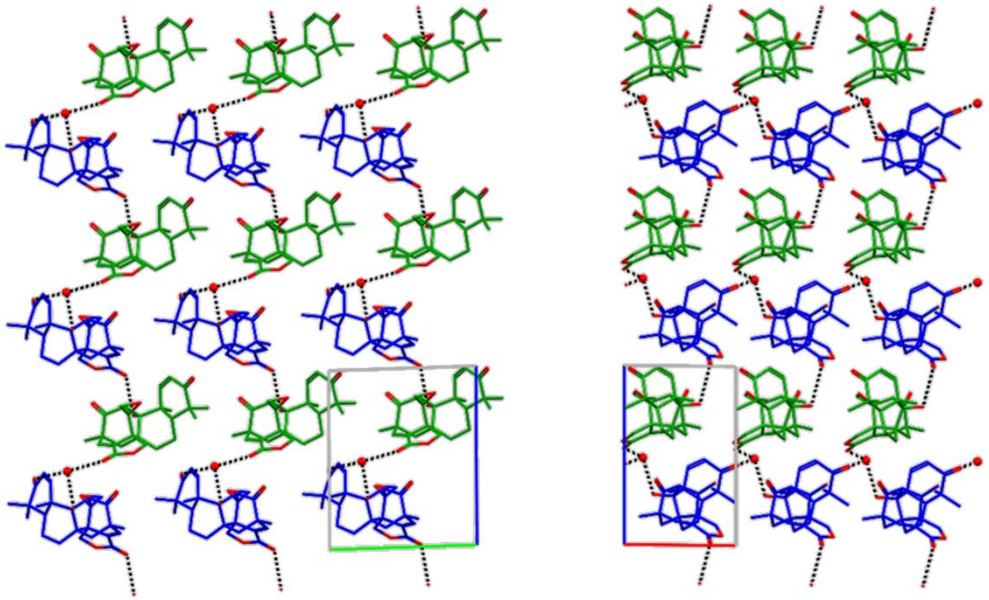


Modulated $P2_1$, *Z'*=1 structure
angles of the *P*1 cell are 69.7, 69.7, 78.5°
the angles of the basic $P2_1$ cell ([1$\bar{1}$0] unique) are 90.0, 116.6, 90.0°

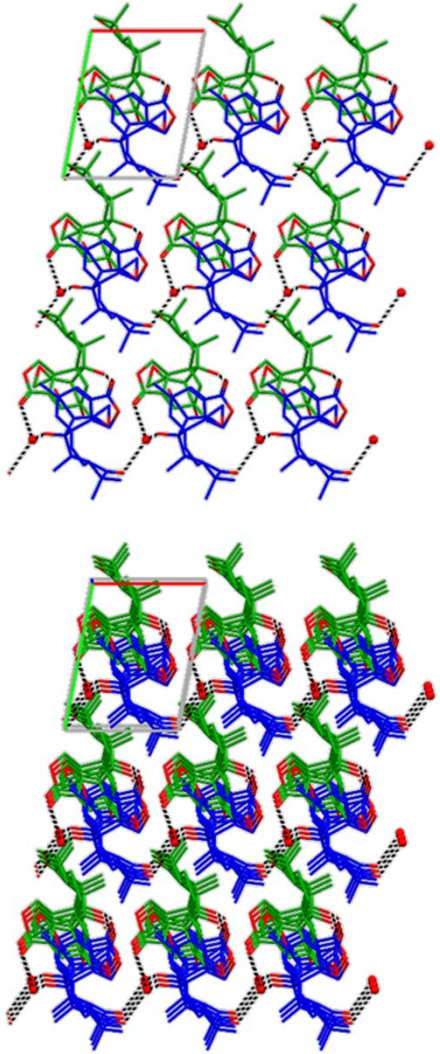
2_1, 3-D (but a mimic because it is a hemihydrate)

NIYQIY
(*P*1, *Z*=2)

Views along **a** and **b**

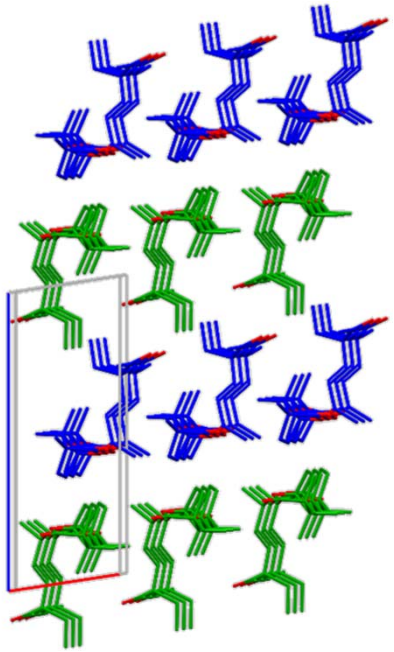


Views along **c** and **c***



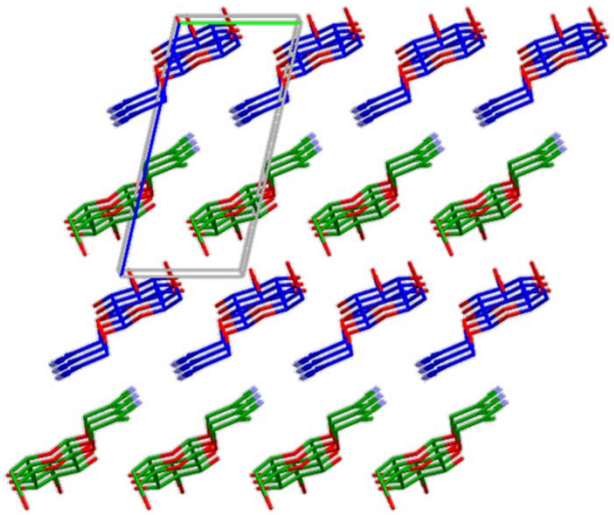
P2_1, *Z'*=1 mimic with **c** unique
(there is only one H_2O molecule for
each pair of larger molecules);
the cell angles are 91.5, 90.4, 100.7°

Examples of distorted $P2_1$ structures; projections are along $\mathbf{a}_i^*$, where $\mathbf{a}_i$ is the unique axis (conventionally $\mathbf{a}_2$), and are three unit cells deep



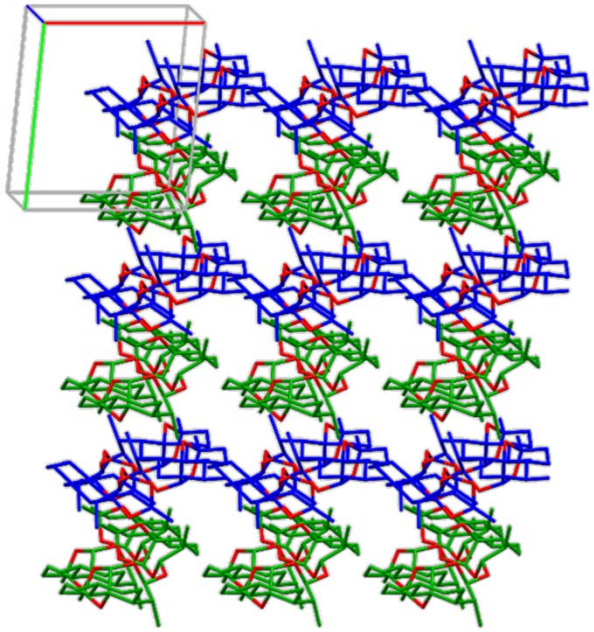
DIDREO

unique axis **b**



EGOZIK

unique axis **a**



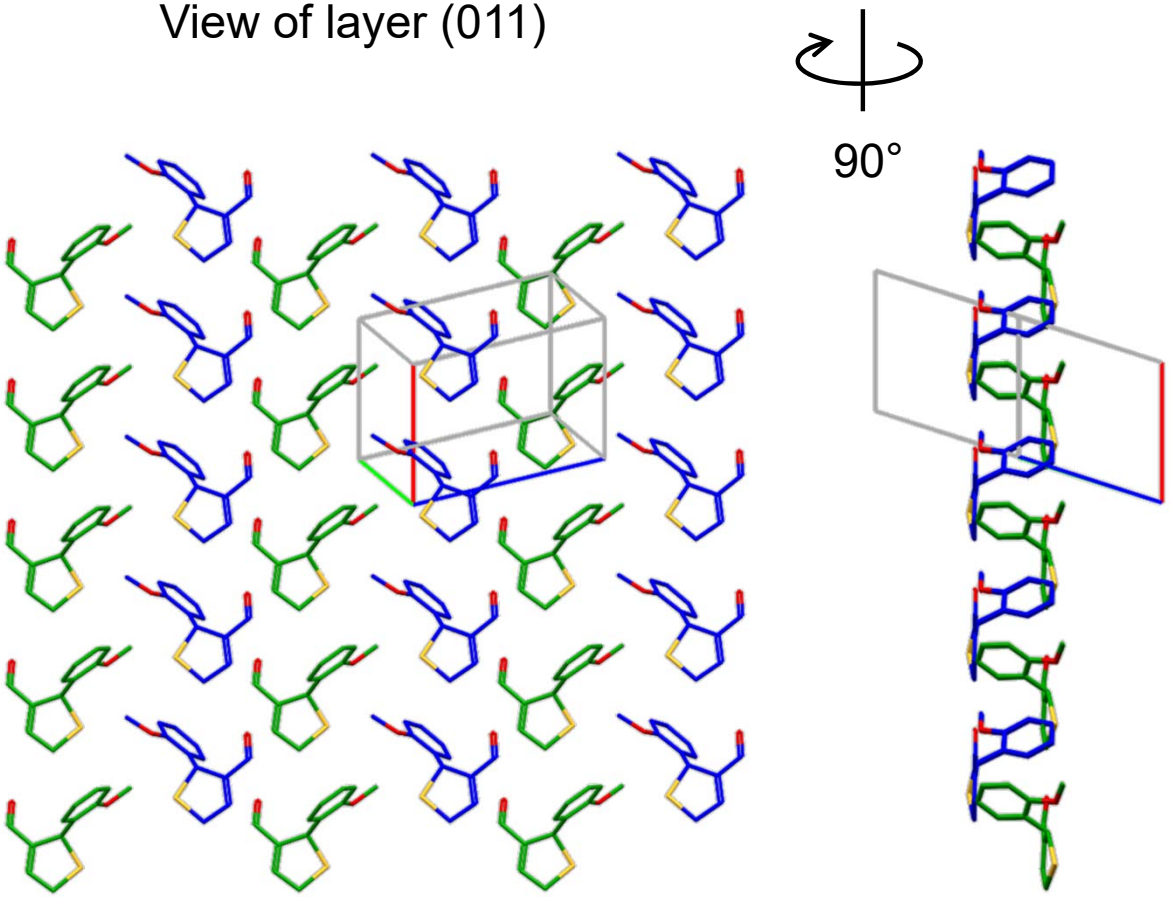
KADMIL

unique axis **c**

2_1, 2-D

DUNHAW
(*P*1, *Z*=2)

View of layer (011)

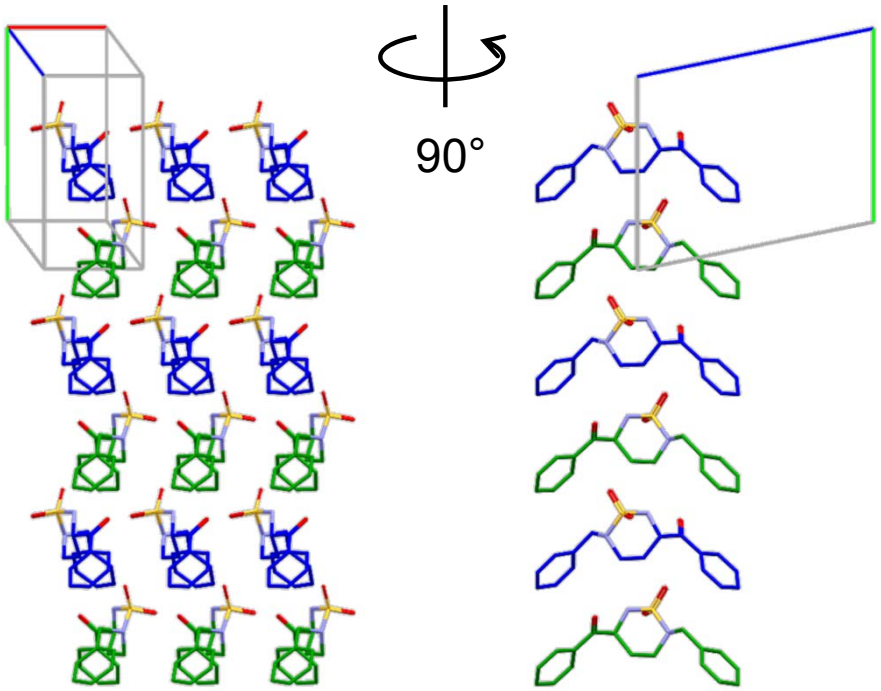


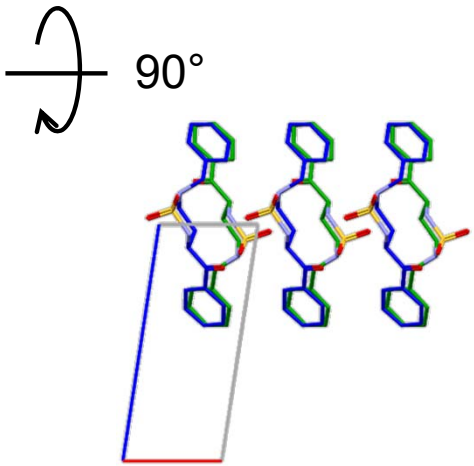
Layer (011)
$p2_111$, z=2, z'=1
axes [001], [010]

2_1, 2-D

GOCQAT
(*P*1, *Z*=2)

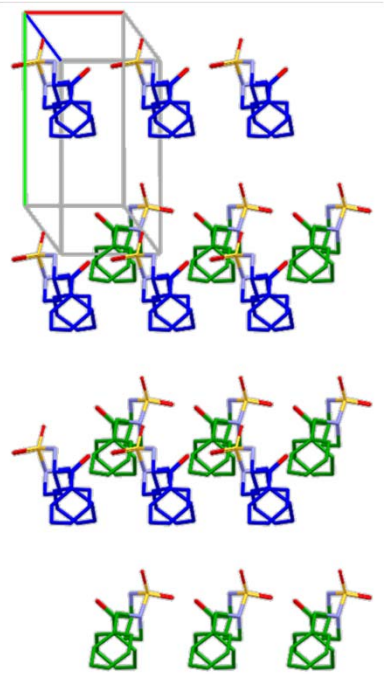
View of layer (001),
½ ≤ *z* ≤ 1½





Layer (001)
p$2_1$11, *z*=2, *z'*=1
axes [010], [100]

View of layer (001),
0 ≤ *z* ≤ 1

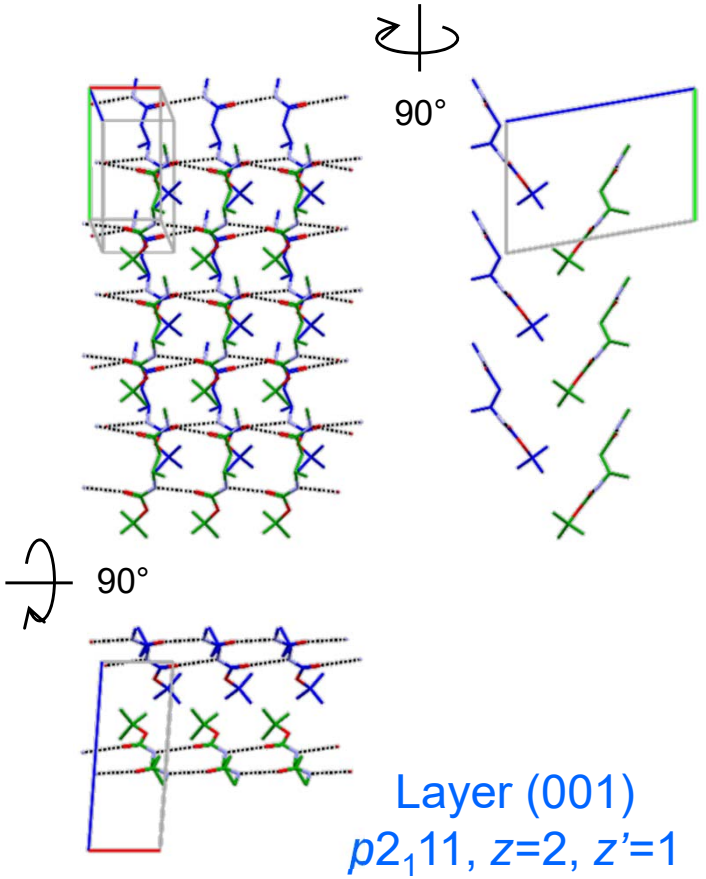


2_1, 2-D

LEFPAO
(*P*1, *Z*=2)

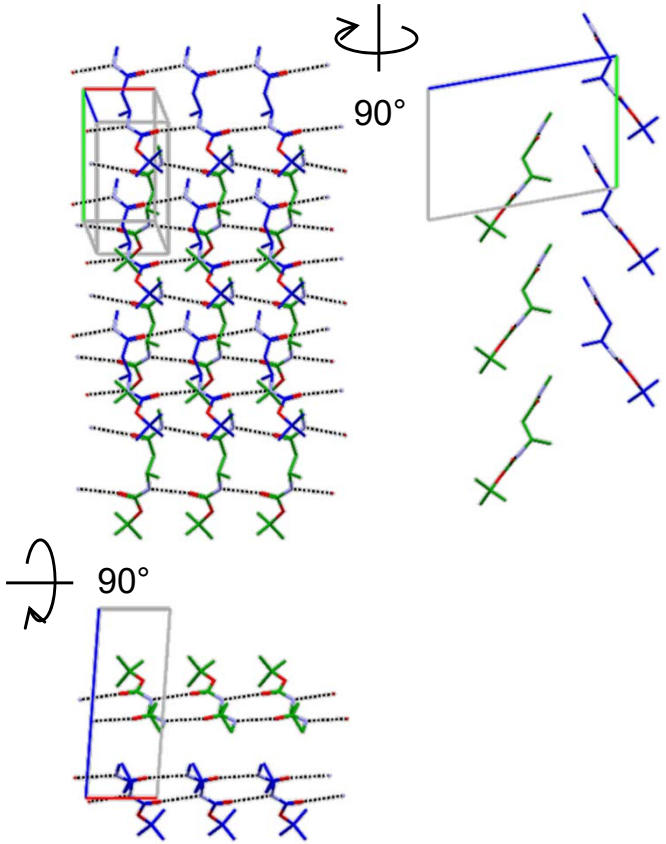
View of layers (001)

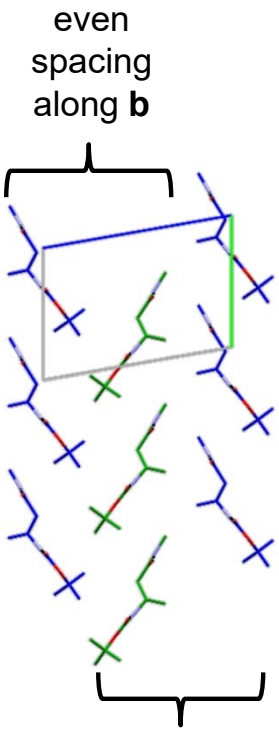
$0 \le z \le 1$
(even spacing
along **b**)



Layer (001)
$p2_111$, z=2, z'=1
axes [010], [100]

$½ \le z \le 1½$
(very uneven
spacing along **b**)

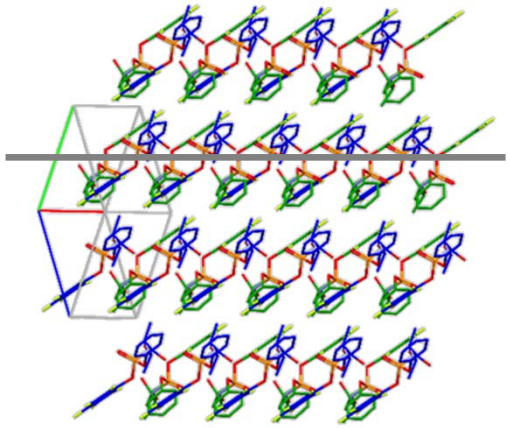




2_1, 2-D

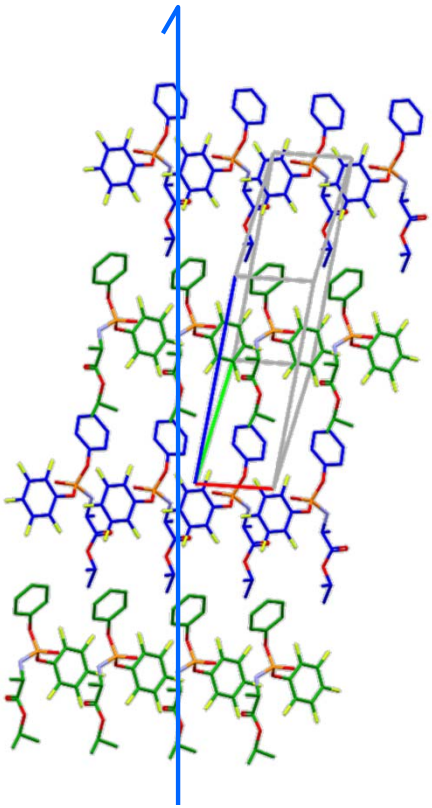
UCIYAI
(*P*1, *Z*=2)

View along $[1\bar{1}\bar{1}]$

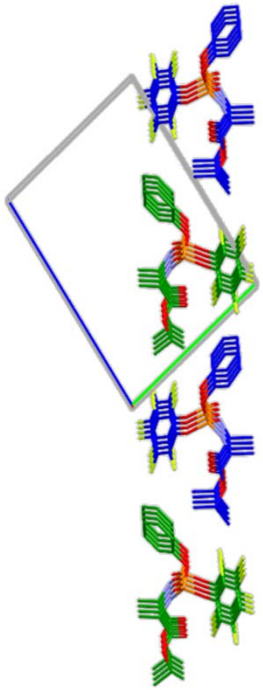


$(01\bar{1})$

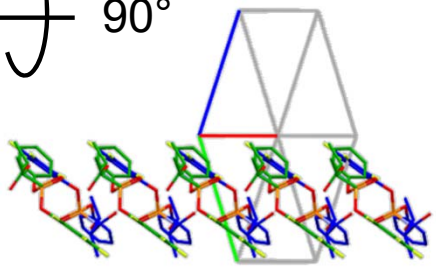
Layer $(01\bar{1})$



90°



90°

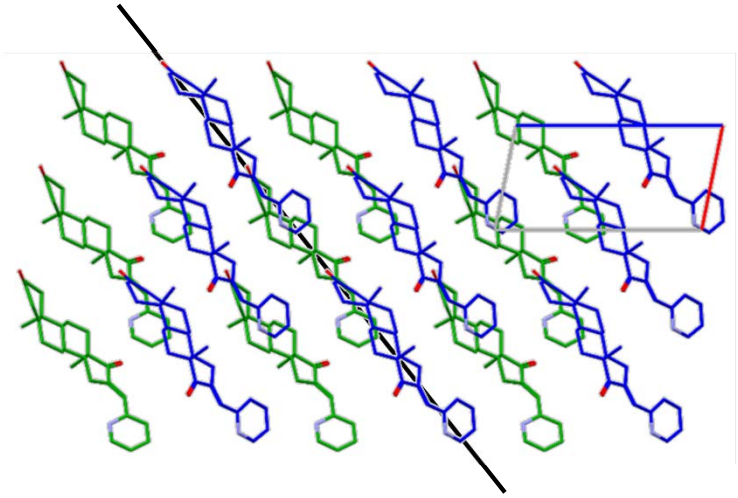


Layer $(01\bar{1})$
$p2_111$, z=2, z'=1
axes $[1\bar{1}\bar{1}]$, [100]

2_1, 2-D

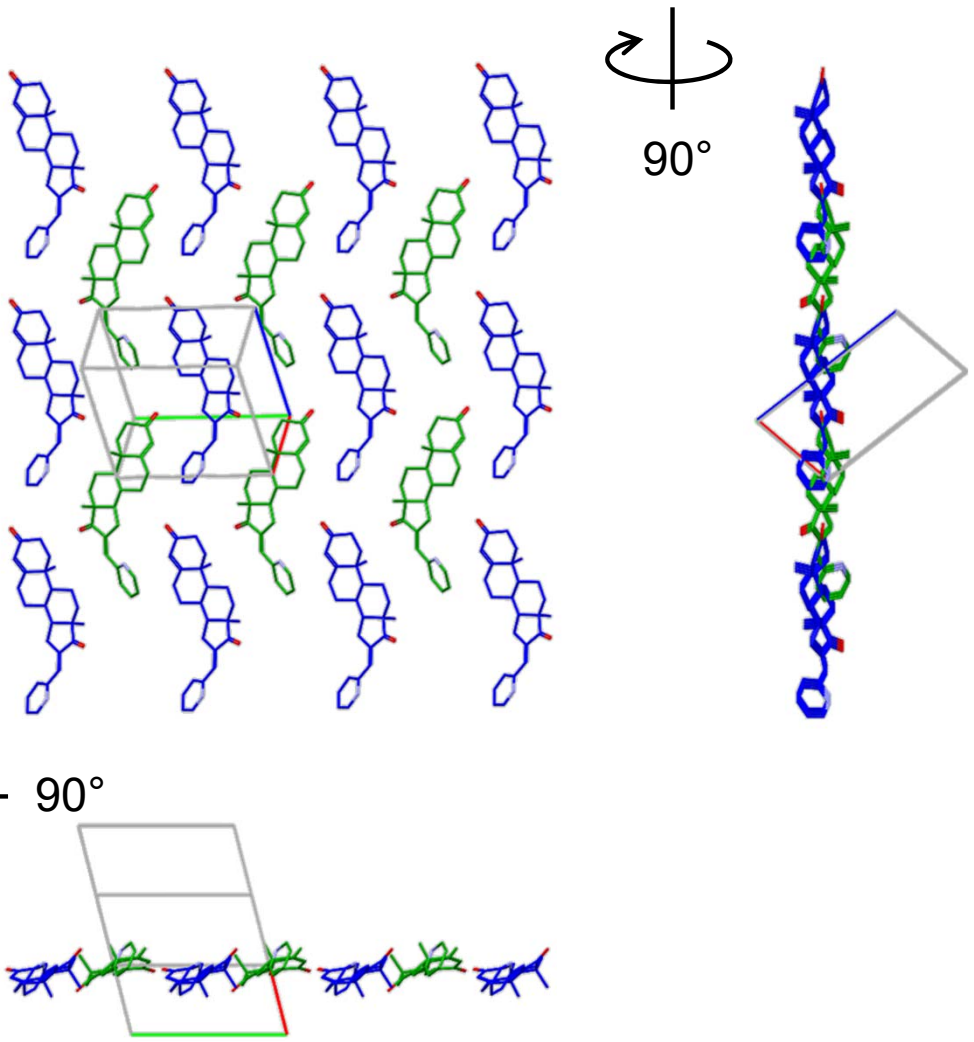
WOYSEI
(*P*1, *Z*=2)

View along **b**



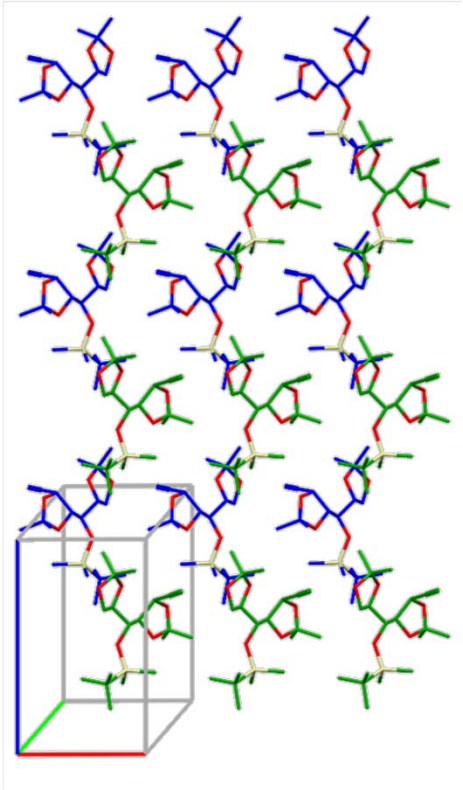
(102)

Layer (102)



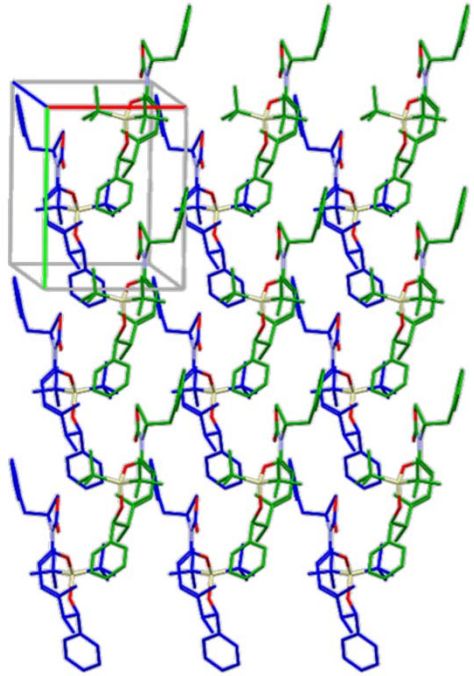
Layer (102)
$p2_111$, z=2, z'=1
axes [20$\bar{1}$], [010]

Additional examples of $p2_111$ (the approximate 2_1 axes are all vertical)



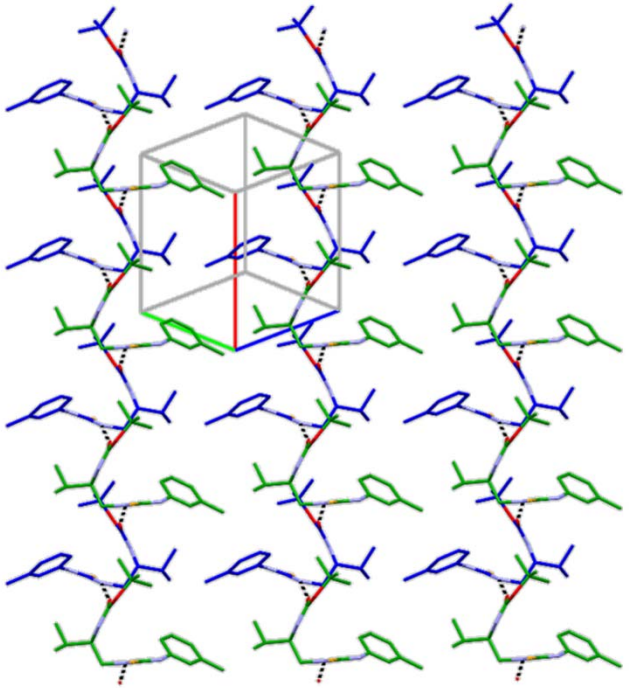
CEFKAA

Layer (010),
axes [001], [100]



ESOPIM

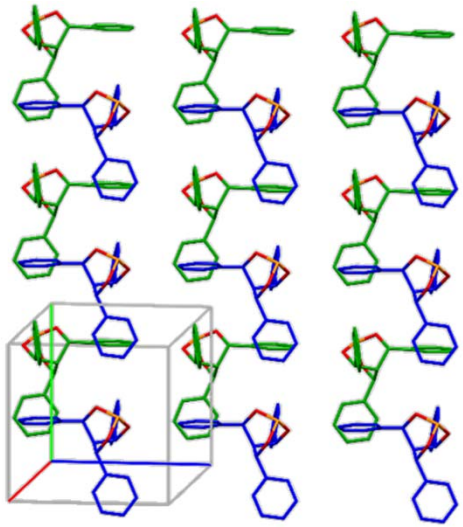
Layer (001),
axes [010], [100]



INAGAH

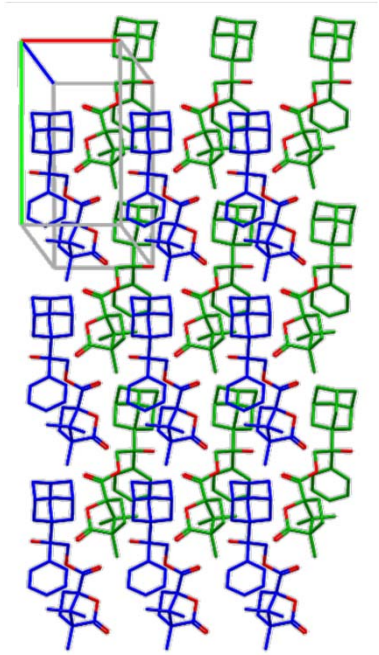
Layer (011),
axes [100], [$01\bar{1}$]

Yet more examples of $p2_111$ (the approximate 2_1 axes are all vertical)



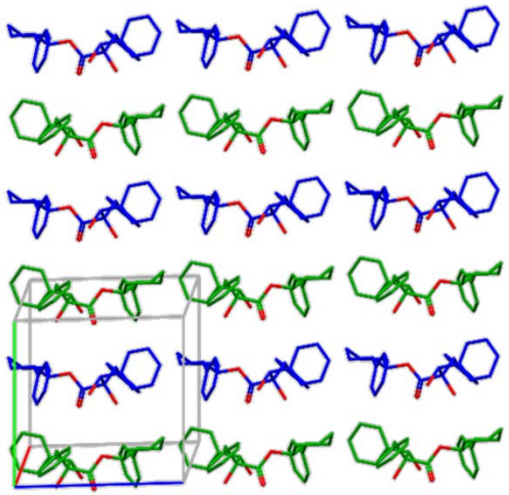
OFEFOW

Layer (100),
axes [010], [001]



REJSUU

Layer (001),
axes [010], [100]



WULSUS

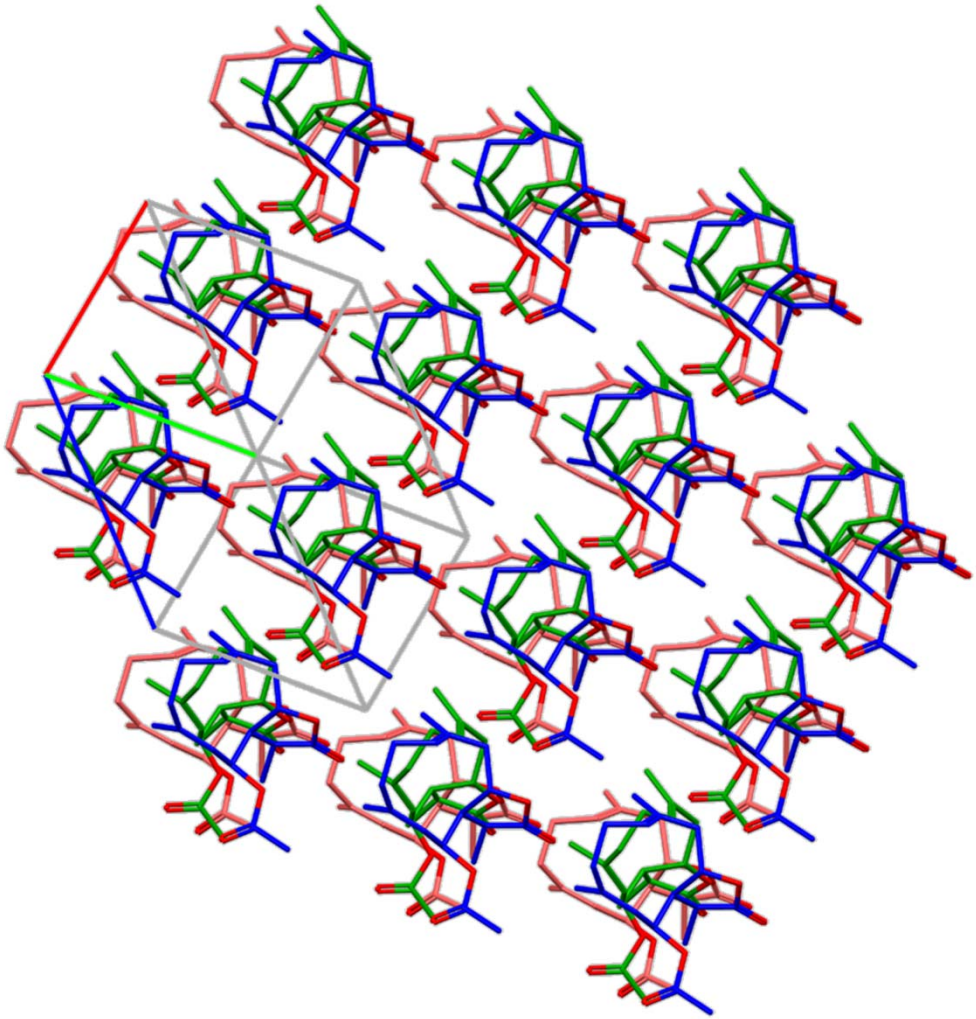
Layer (100),
axes [010], [001]

Structure that has an approximate translation

approximate translation

ATUTOA
(*P*1, *Z*=3)

View along [$1\bar{1}1$]



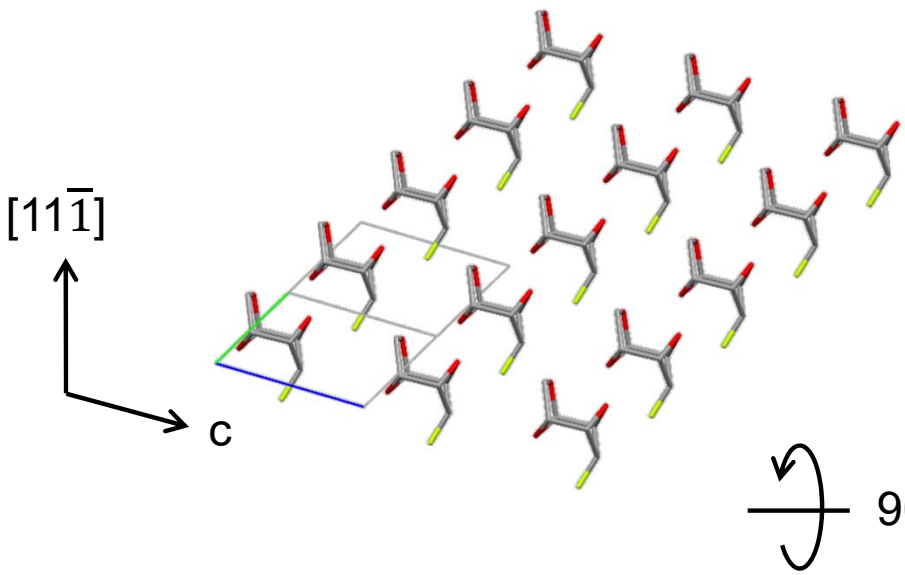
Approximate translation [$1\bar{1}1$]/3 (more approximate than most)

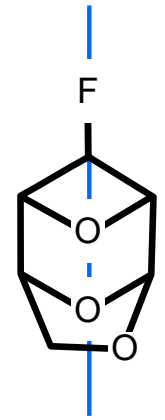
Structures that have more than one type
of approximate symmetry

Im mimic, 3-D

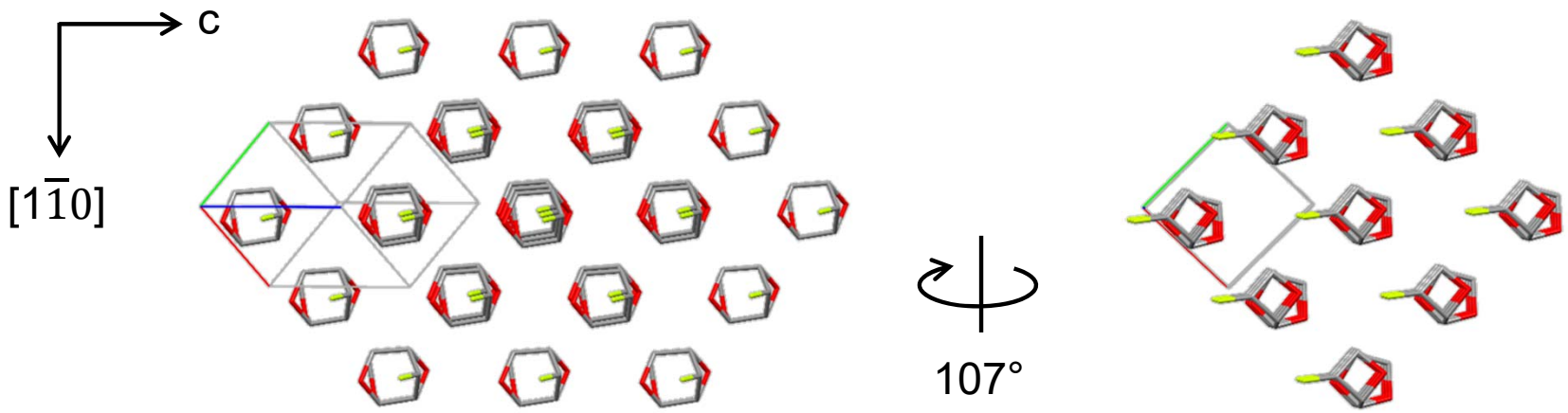
BAPGIK
(*P*1, *Z*=1)

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





Im, *Z*=2, *Z'*=½
axes [00$\bar{1}$], [1$\bar{1}$0], [$\bar{1}\bar{1}$1];
angles 88.4, 107.3, 90.3°

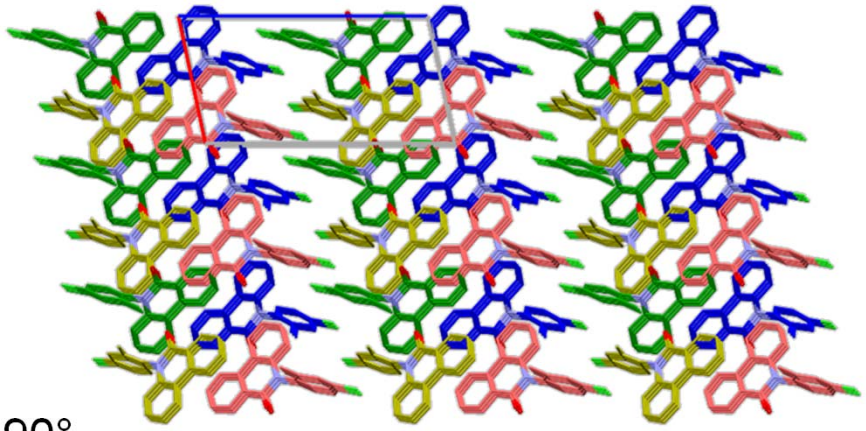


$P2_1/a$ mimic , 3-D

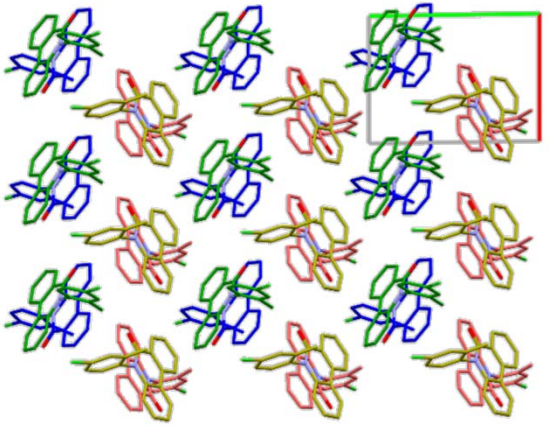
BIZPAE
($P1$, Z=4)

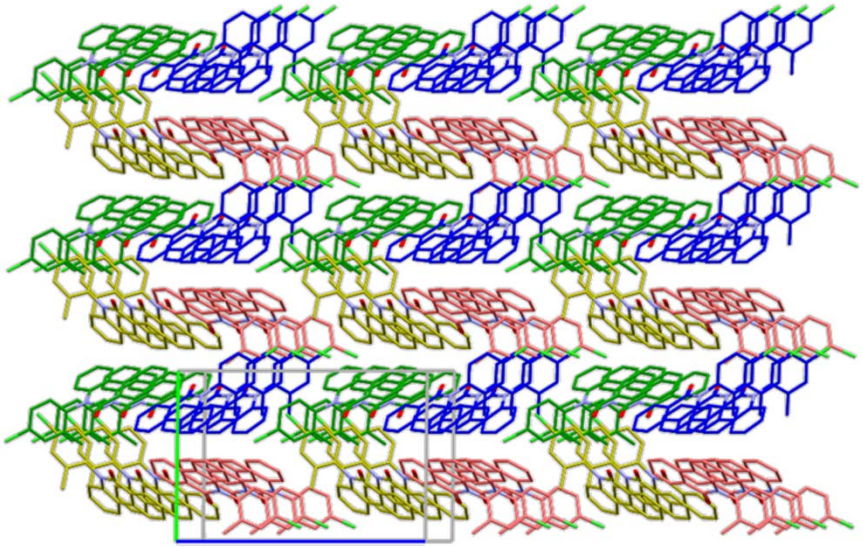
View along **b***

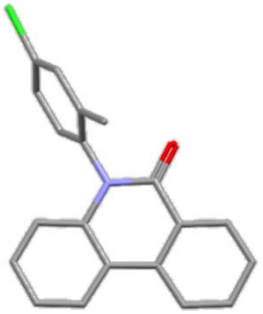
90°



90°





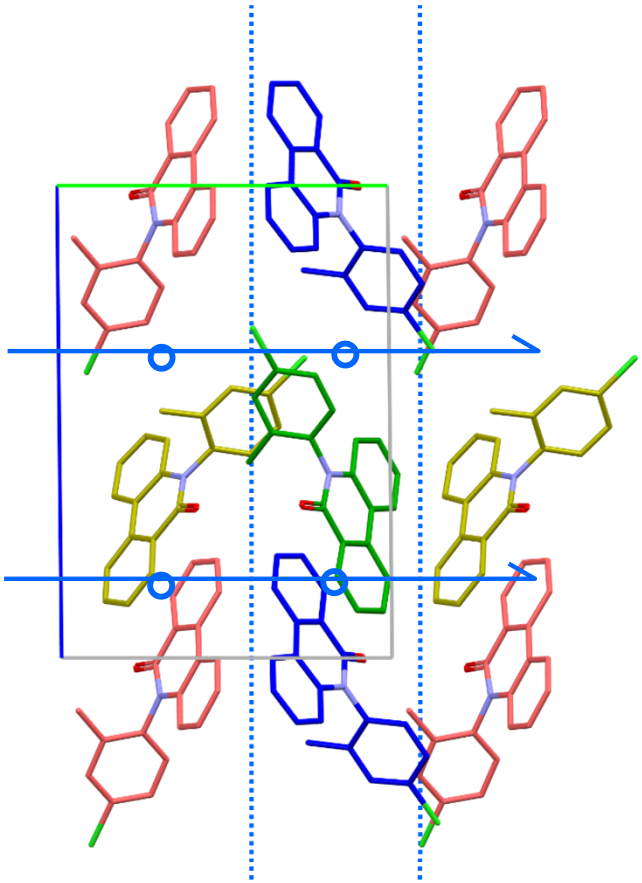


The inversion and glide relationships are approximately correct for all atoms except the Me group. Cell angles are 89.2, 78.0, and 89.0°

(see also next page)

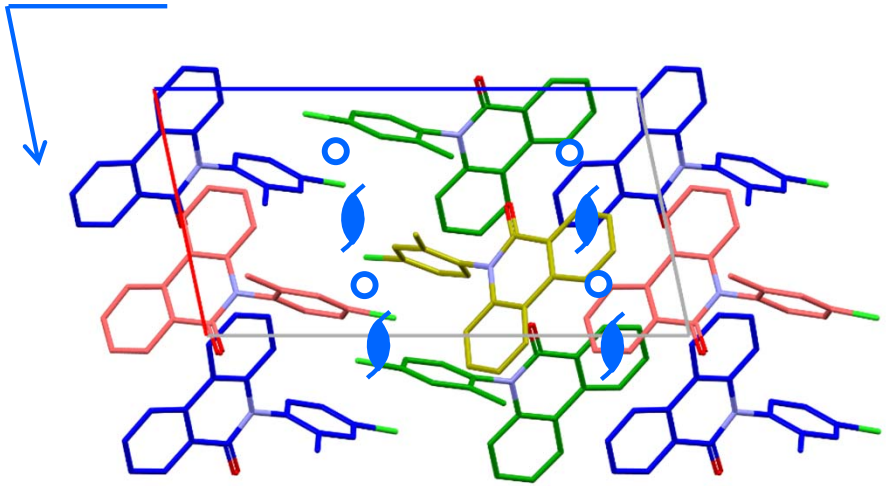
$P2_1/a$ mimic, 3-D

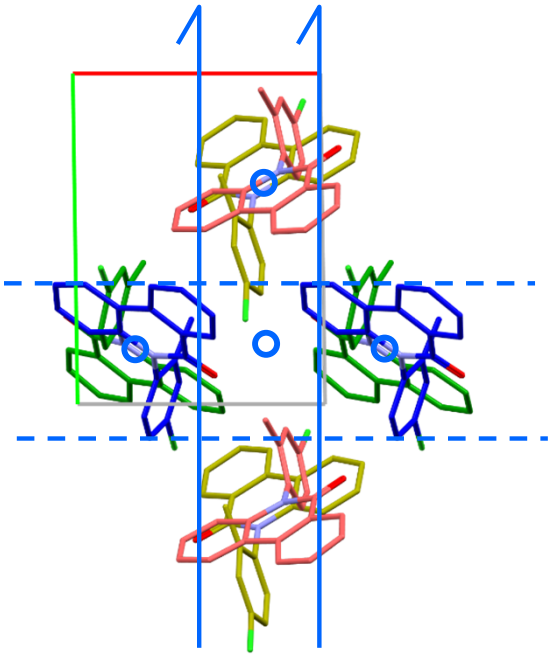
Views along **a**, **b**, and **c**



While the inversion and glide relationships are approximately correct for all atoms except the Me group the deviations are obvious

BIZPAE, con't ($P1$, Z=4)

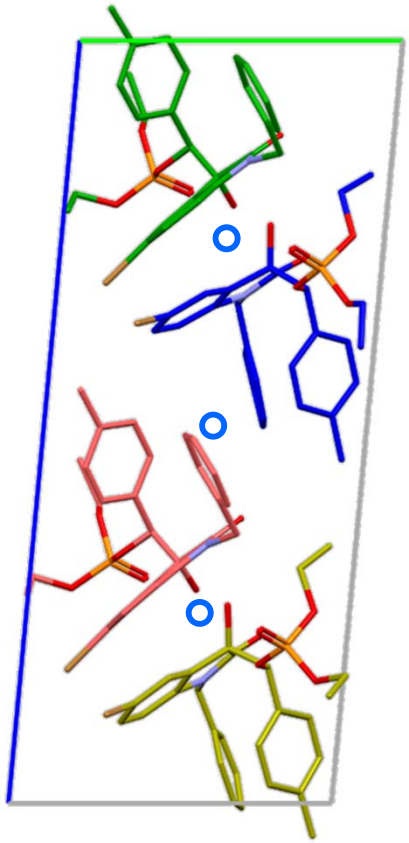


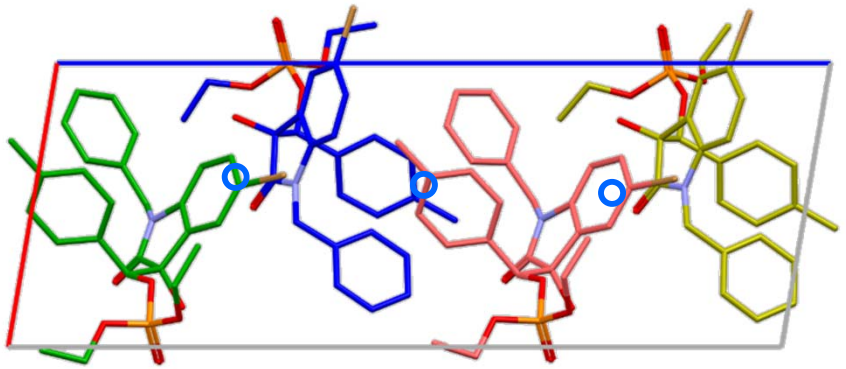


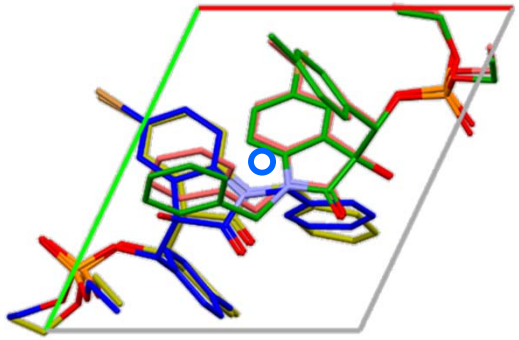
$P\bar{1}$ mimic with an approximate translation (**c'**=**c**/2), 3-D

BUPCAS
(*P*1, *Z*=4)

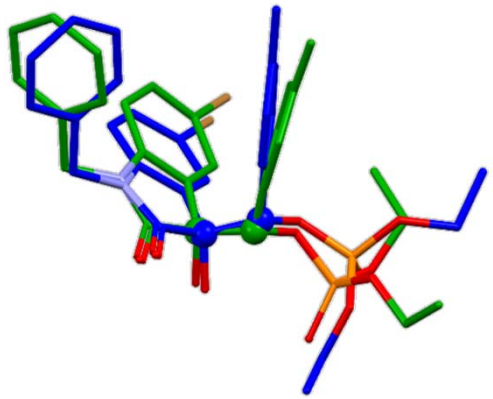
Views along **a**, **b**, and **c**







Approximate **c**/2 translation

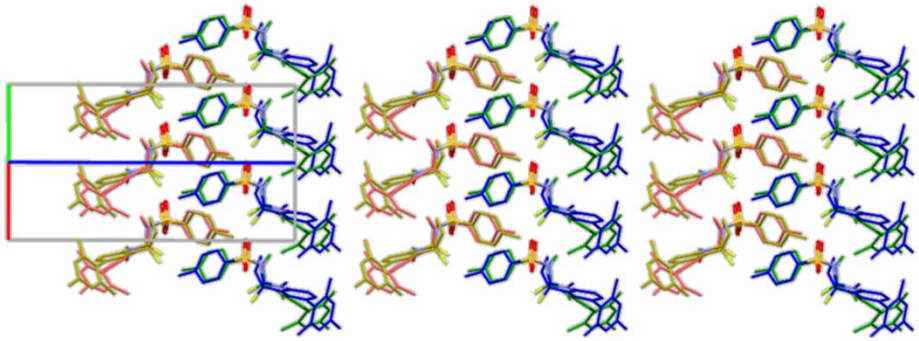


Overlay of molecules in approximate dimer

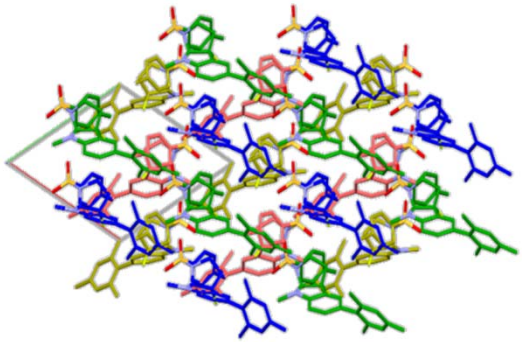
distorted $P2_1$ with an approximate translation (**b**' = $[1\bar{1}0]/2$), 3-D

IYAVEK
($P1$, Z=4)

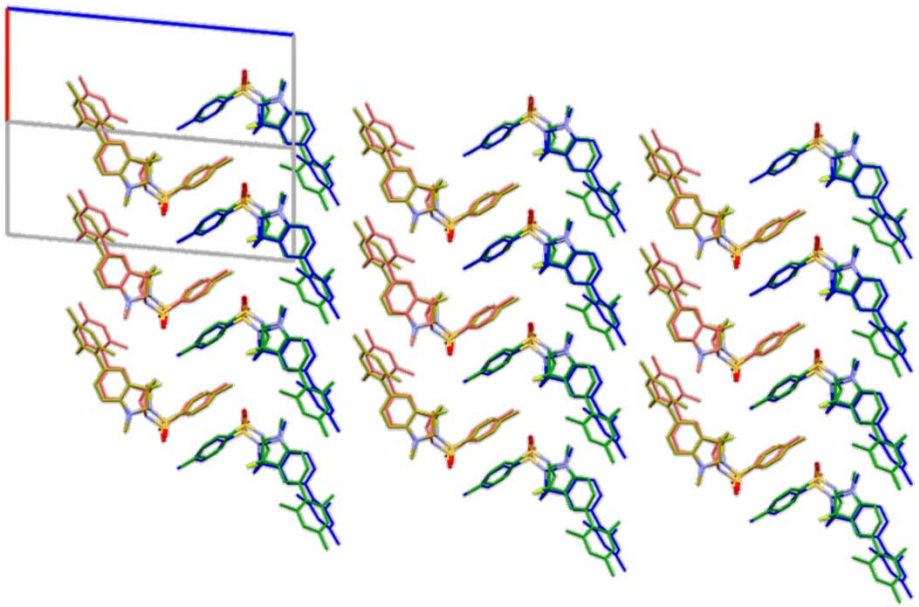
View along [110]



90°



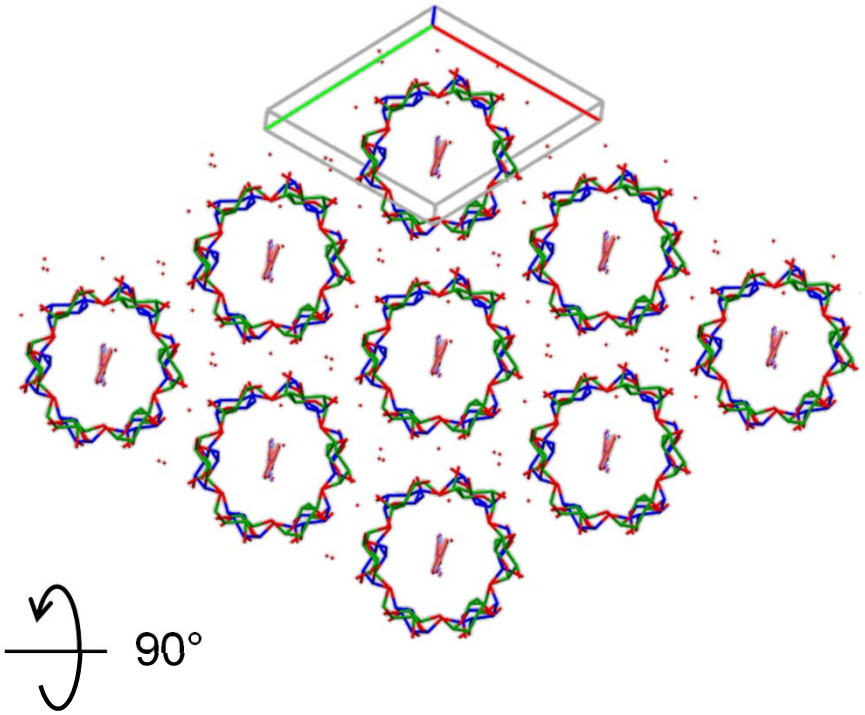
90°

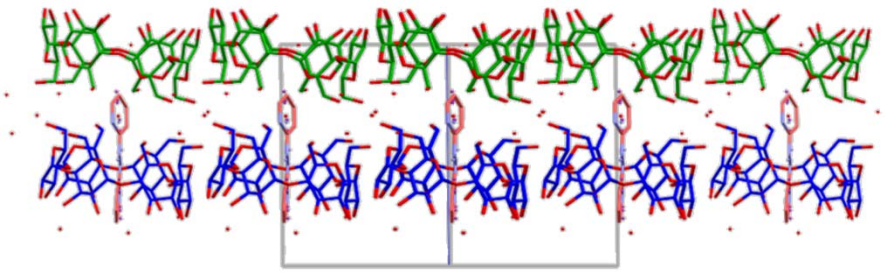


$P2_1$ cell with axes
$[110]/2$, $[1\bar{1}0]/2$, $[00\bar{1}]$
has angles
90.0, 95.3, and 90.1°

distorted *P*622, 3-D

Layer (001)



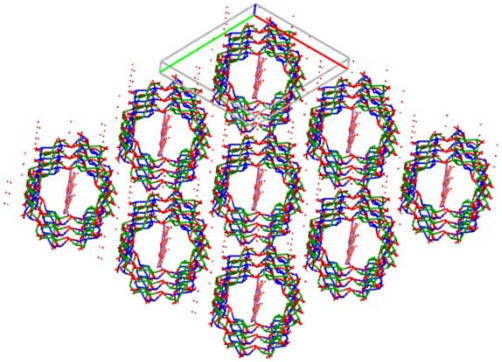


QACCII
(*P*1, *Z*=2)
(a cyclo-
dextrin
complex)

a=13.70, *b*=13.97 Å,
γ=118.7°,
α=93.2, β=91.9

α, β are close enough to 90°
that the approximate symmetry
should be considered to be 3-D

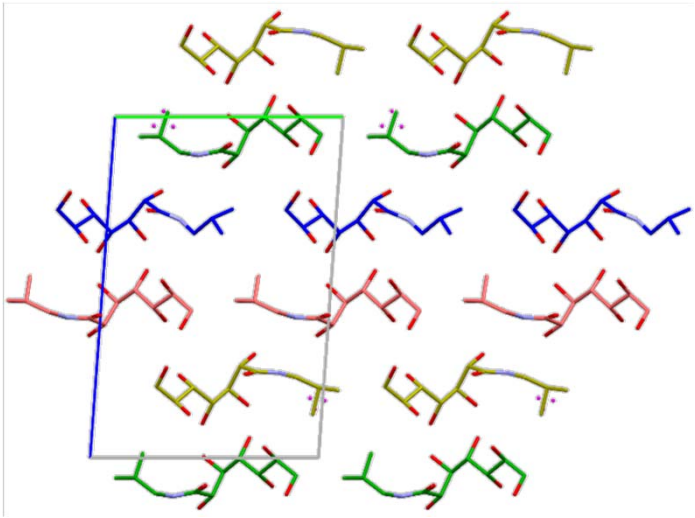
View along **c***



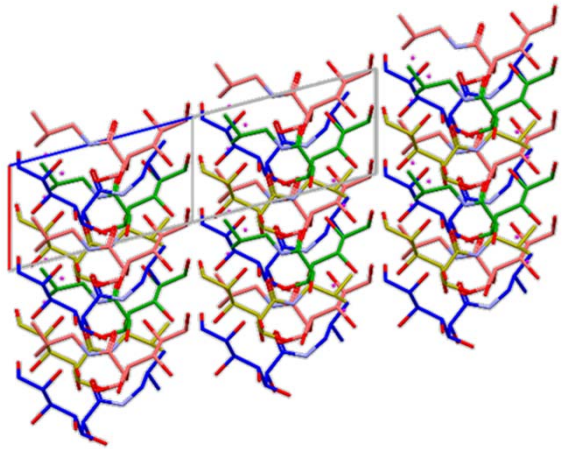
distorted *C*2 with an approximate translation (**c**'=[111]/2), 3-D

WEYZOQ
(*P*1, *Z*=4)

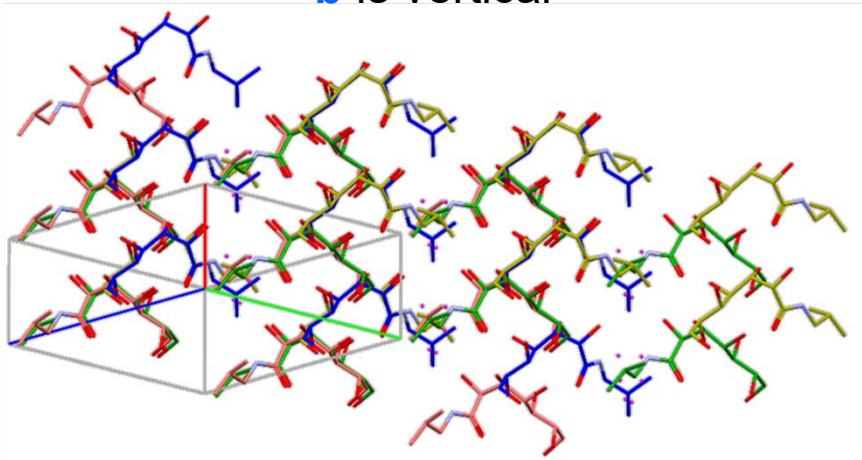
View along **b** = -**a**



View along **a** = [01$\bar{1}$];
b is vertical



View along **c** = [½½½];
b is vertical

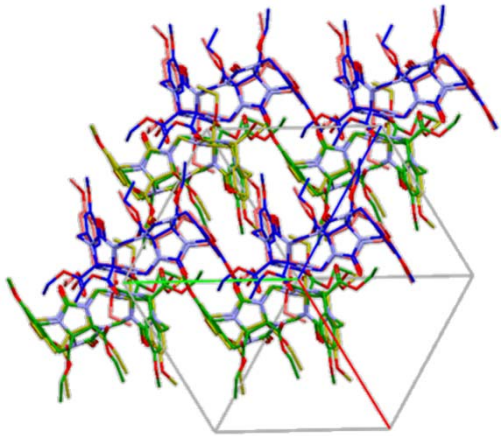


*C*2,
axes [01$\bar{1}$], [$\bar{1}$00], [½½½];
angles 90.9, 112.6, and 90.5°

distorted $P\bar{1}$ with an approximate translation (**a'**=[111]/2), 3-D

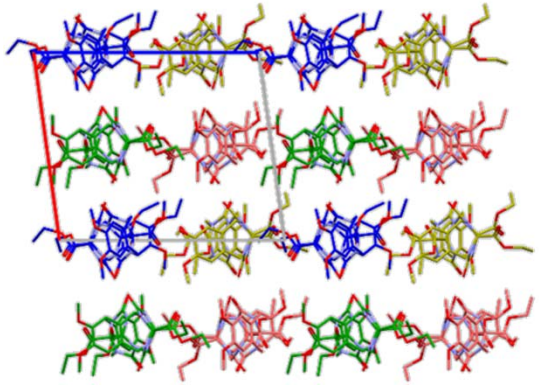
XEQTUI
(*P*1, *Z*=4)

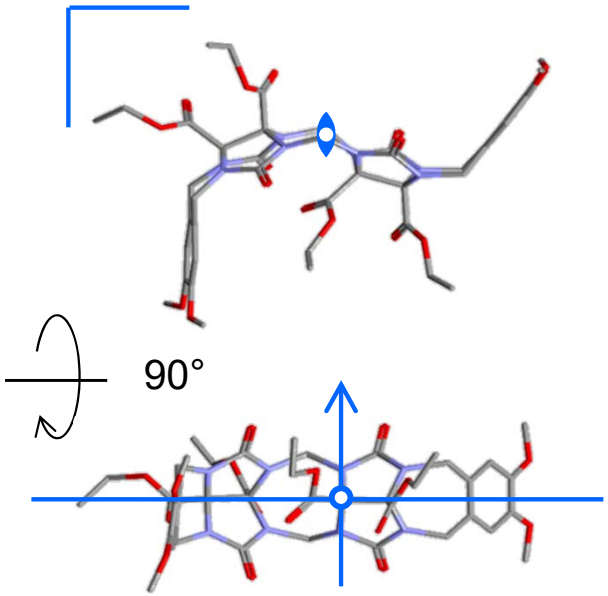
View along [111]

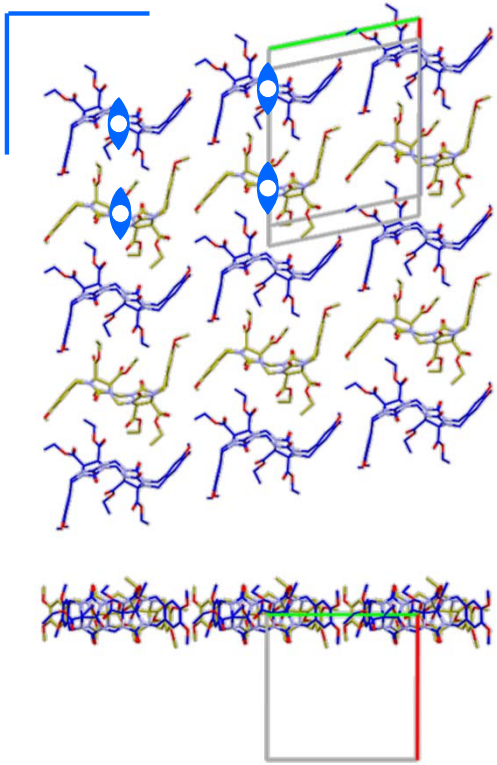


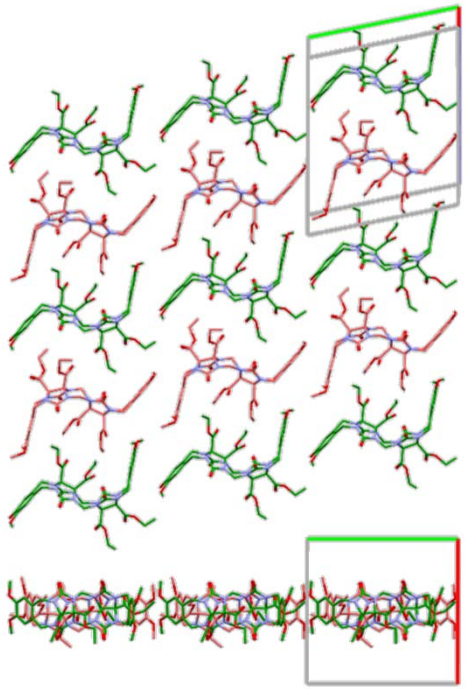
Layers (100)
*p*112/*m*, *z*=2, *z'*=½
(approximate 3-D
symmetry $P\bar{1}$ with
translation [111]/2)

View along **b**





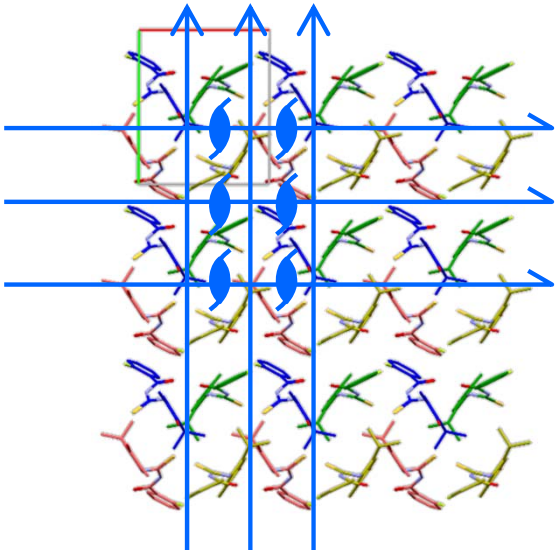




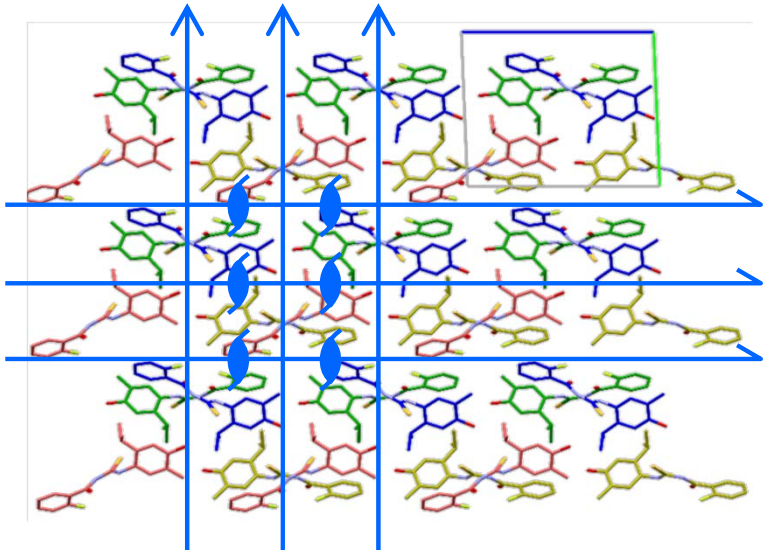
distorted $P2_12_12$, 3-D

ZEBVEJ
($P1$, Z=4)

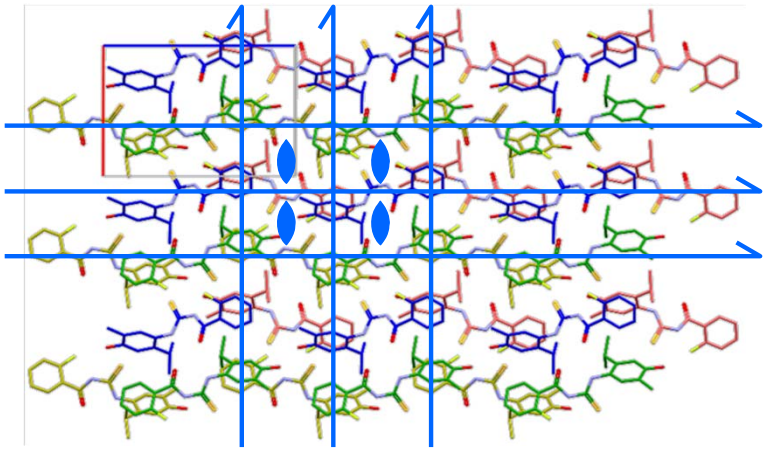
View along **a** = **c**
c (the approximate 2) is vertical



View along **b** = **a**
c is vertical



View along **c** = **b**



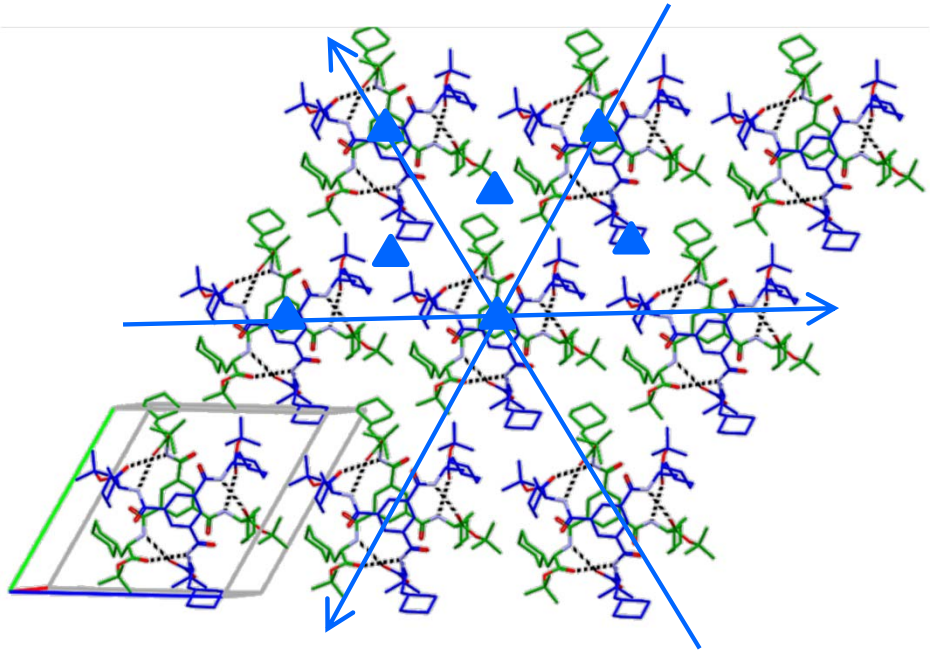
Angles in the $P2_12_12$ cell are 90.2, 92.3, and 90.1°

distorted *p*321, 2-D

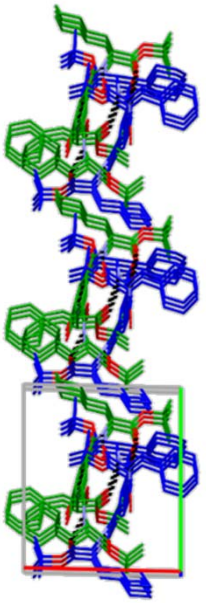
Molecule can have threefold symmetry

AZALIY
(*P*1, *Z*=2)

Layer (100)

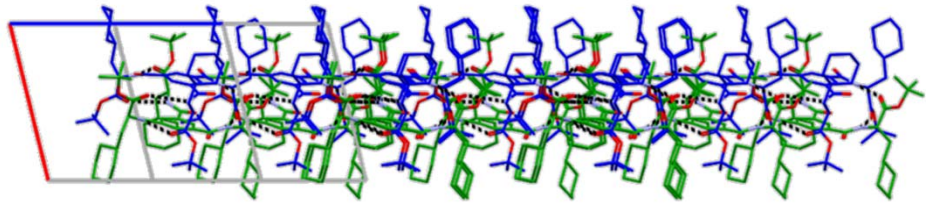


90°



Layer (100)
*p*321, *z*=2, *z'*=⅓
axes [010], [001]
(*a*=15.8, *b*=15.9 Å;
γ=61.7°)

90°

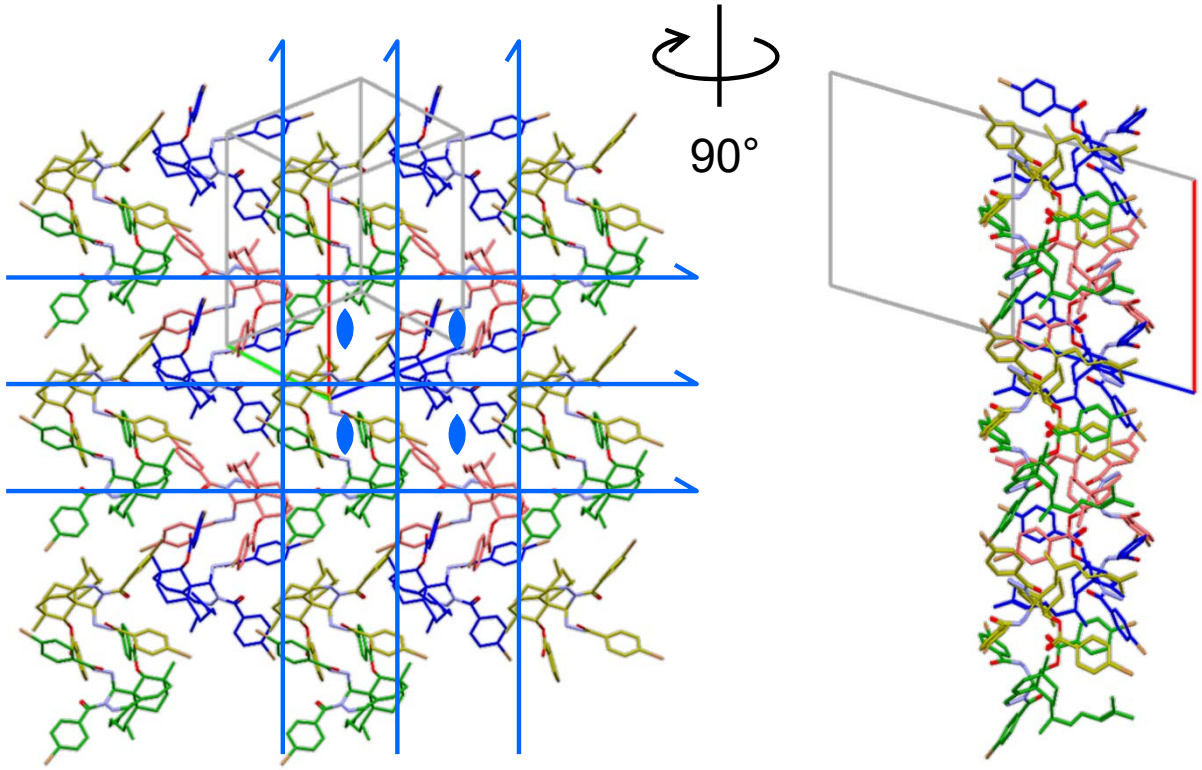


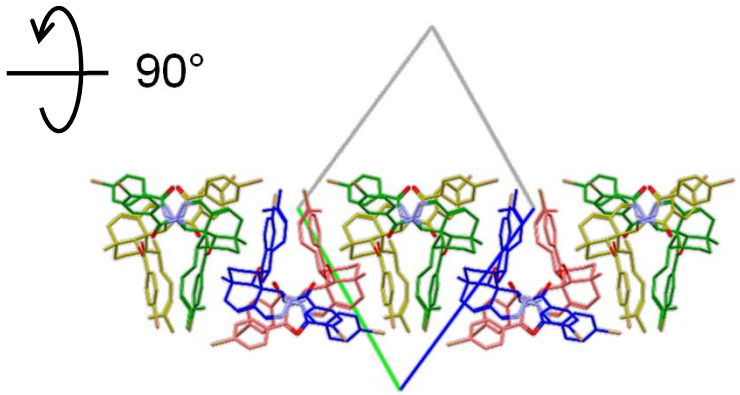
The distortions from *p*321 symmetry are significant but the approximate symmetry is still easy to recognize

distorted $p2_12_12$, 2-D

BIHVUJ
($P1$, Z=4)

Layer (011)



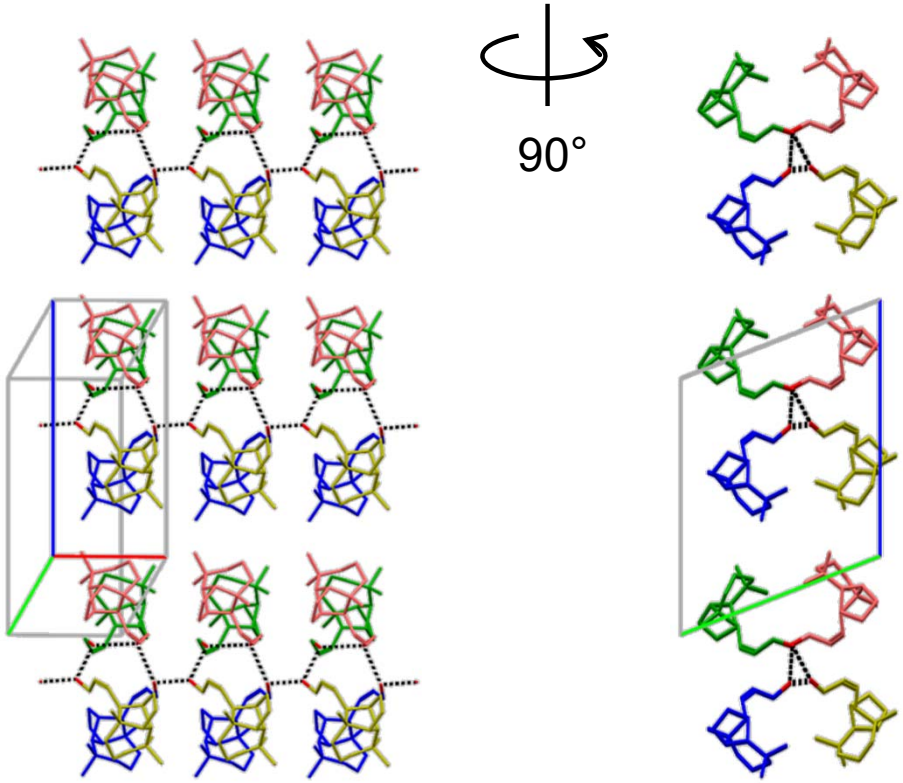


Layer (011)
$p2_12_12$, z=4, z'=1
axes [100], [01$\bar{1}$],
angle 90.7°

distorted *p*222, 2-D

BIVLIC
(*P*1, *Z*=4)

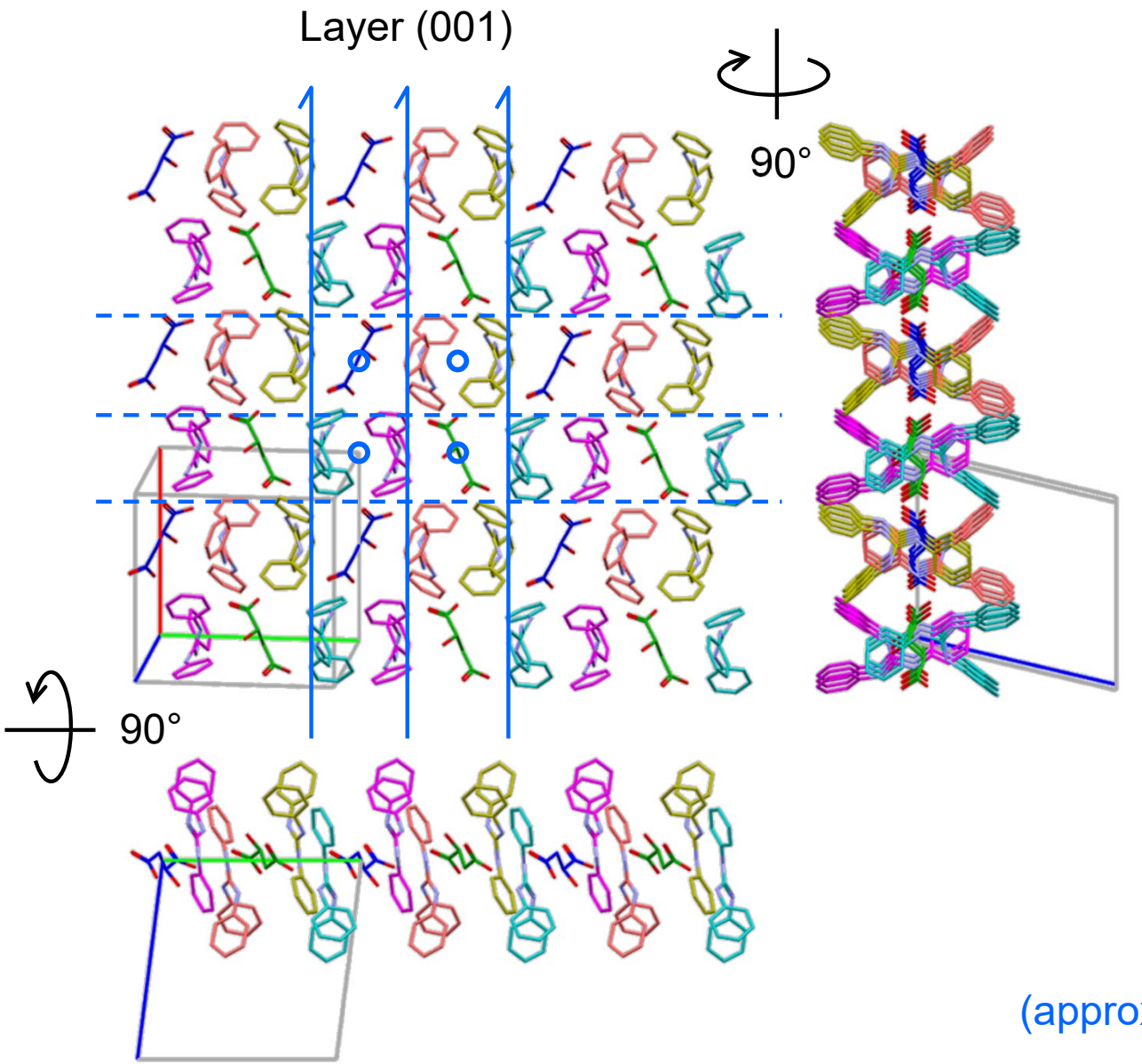
Layer (010)



Layer (010)
*p*222, *z*=4, *z'*=1,
axes [001], [100],
angle 90.5°

$p2_1/b11$ mimic, 2-D
(achiral cation, chiral anion)

CIMCIN
(*P*1, *Z*=2)
(2:1 salt)

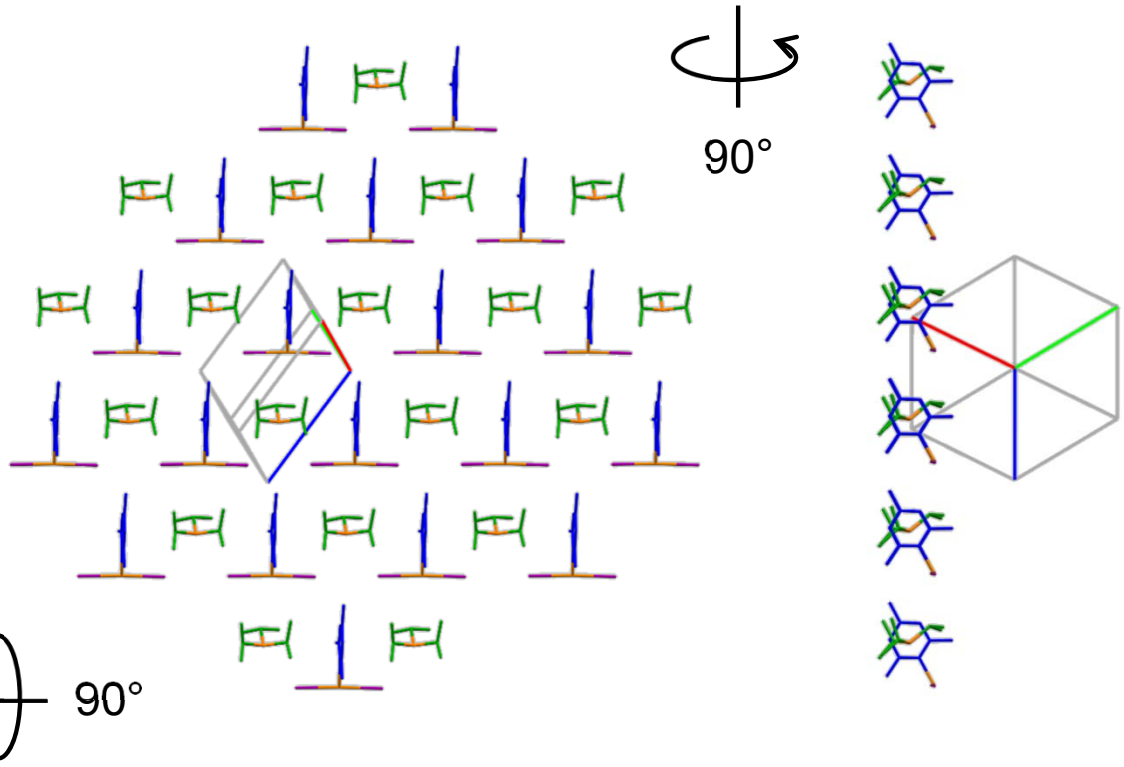


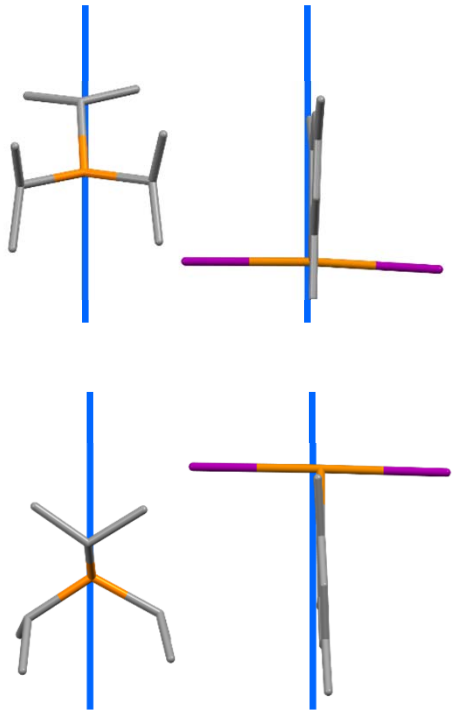
Layer (001)
$p2_1/b11$, z=2, z'=½
axes [100], [010],
angle 91.6°
(approximate 3-D symmetry $P\bar{1}$)

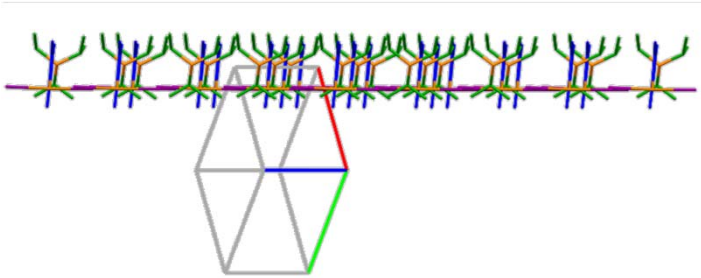
distorted *cm*11, 2-D (achiral)

DOXHIJ
(*P*1, *Z*=1)

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





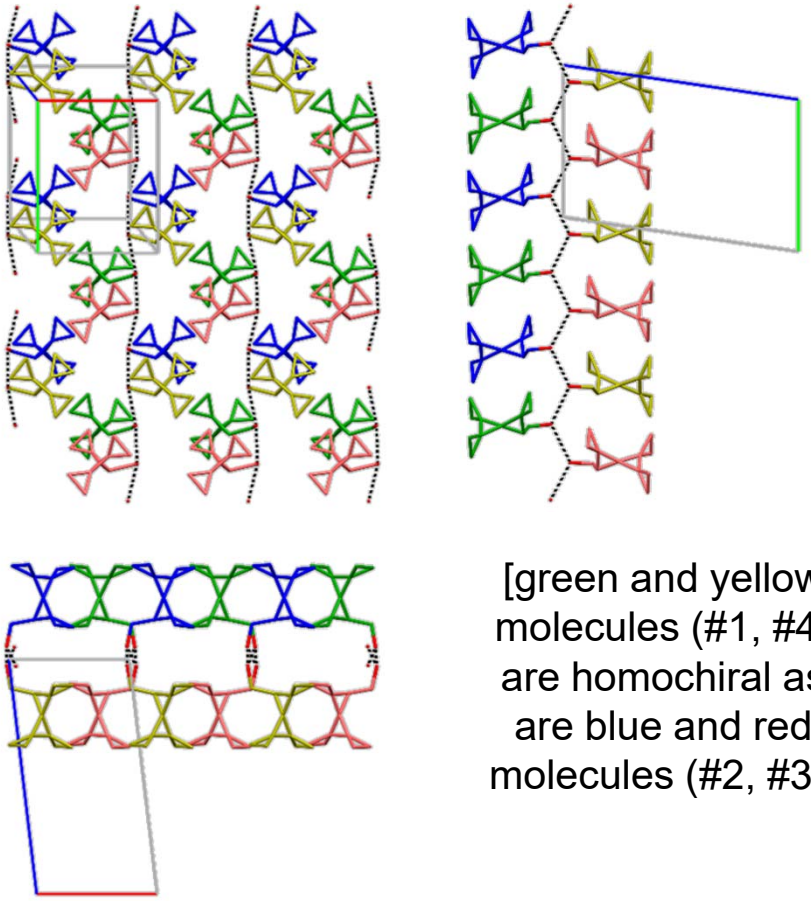


Layer (1$\bar{1}$0)
cm, *z*=2, *z'*=½
axes [111], [11$\bar{1}$],
angle 94.0°

distorted $pb2_1a$, 2-D (a kryptoracemate)
(illustrates problem of the choice of boundaries)

KOVBIG
($P1$, Z=4)

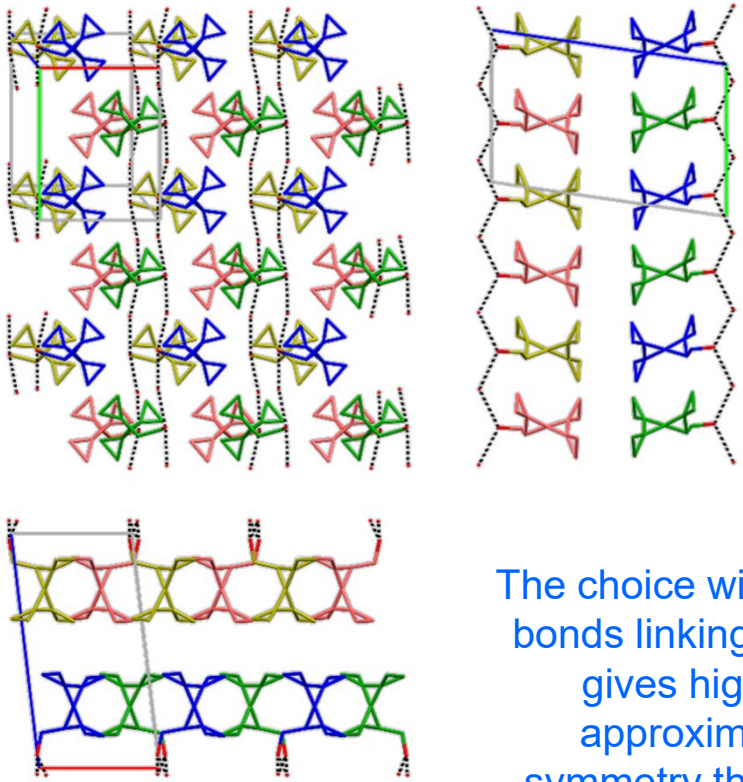
Layer (001), ½ ≤ z ≤ 1½
H bonds lie within layer



[green and yellow molecules (#1, #4) are homochiral as are blue and red molecules (#2, #3)]

Two layers, each $pb11$,
axes [100], [010], angle 90.0°

Layer (001), 0 ≤ z ≤ 1
H bonds link layers (001)



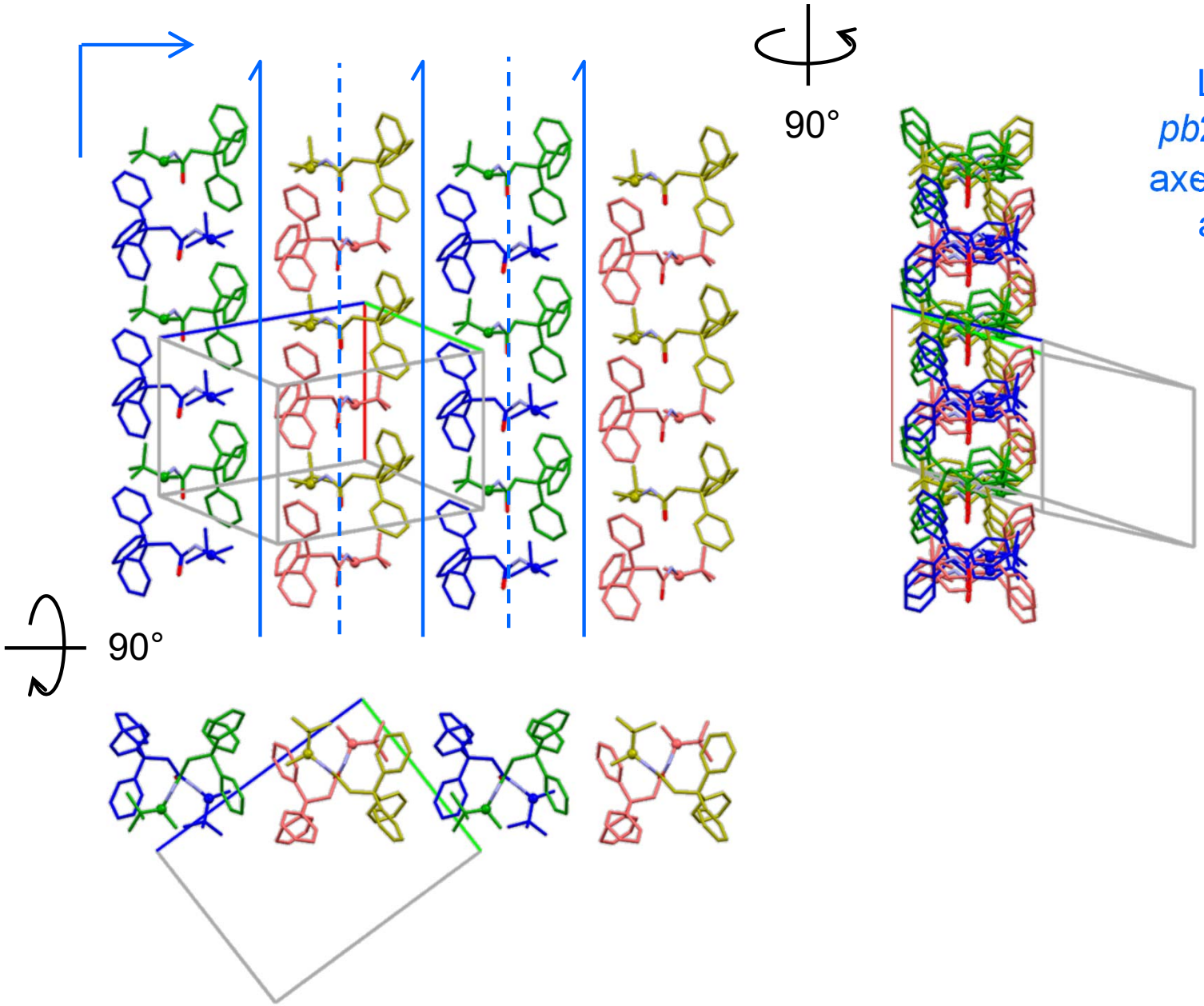
The choice with the H bonds linking layers gives higher approximate symmetry than the choice with H bonds lying within the layers

One layer $pb2_1a$,
axes [100], [010], angle 90.0°

*pb*2$_1$*a* mimic, 2-D

LONJEG
(*P*1, *Z*=4)

Layer (001)

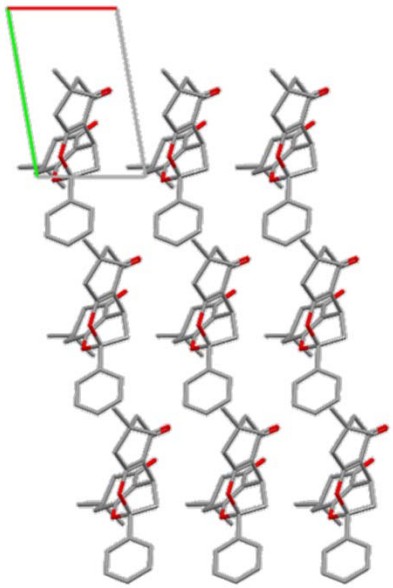


Layer (001)
*pb*2$_1$*a*, *z*=4, *z'*=1
axes [01$\bar{1}$], [100],
angle 87.5°

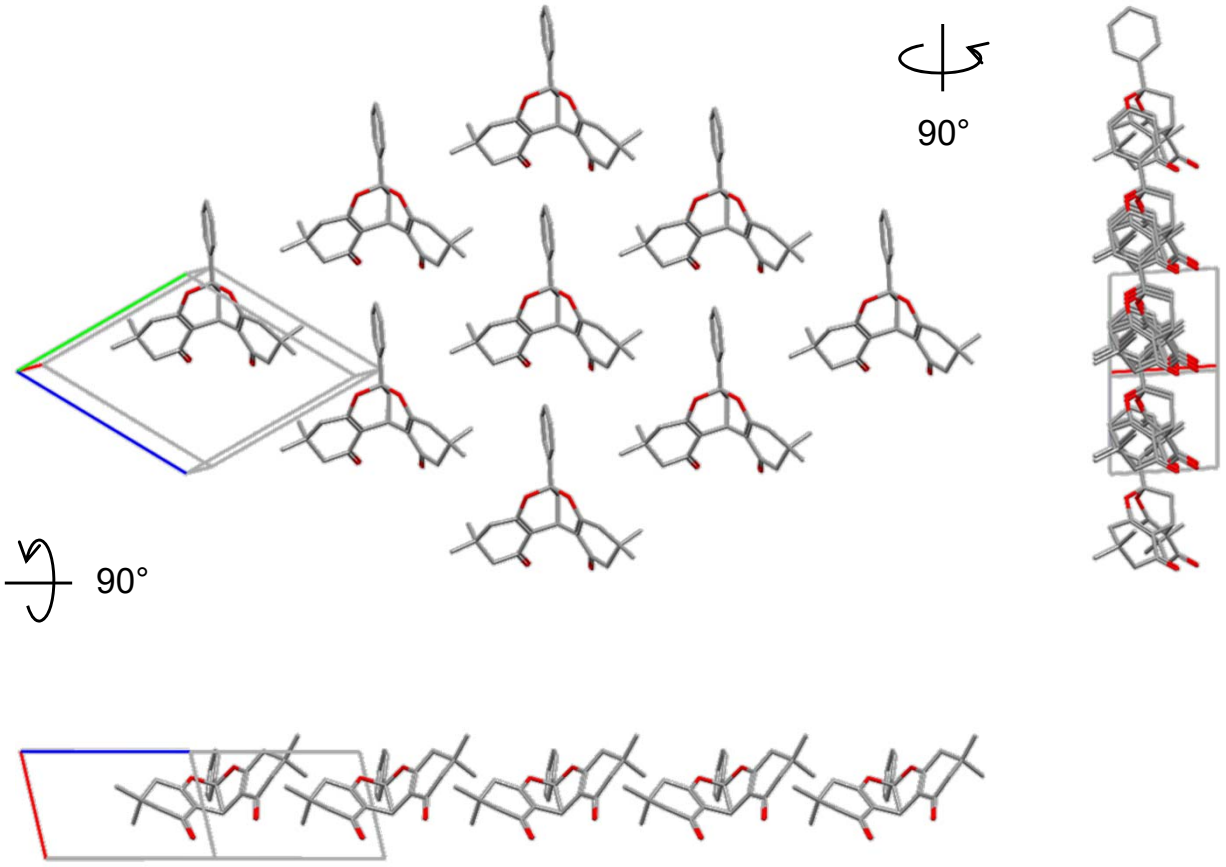
distorted *cm*11, *z'*=½, 2-D (achiral)

PUYPAC
(*P*1, *Z*=1)

View along [001]



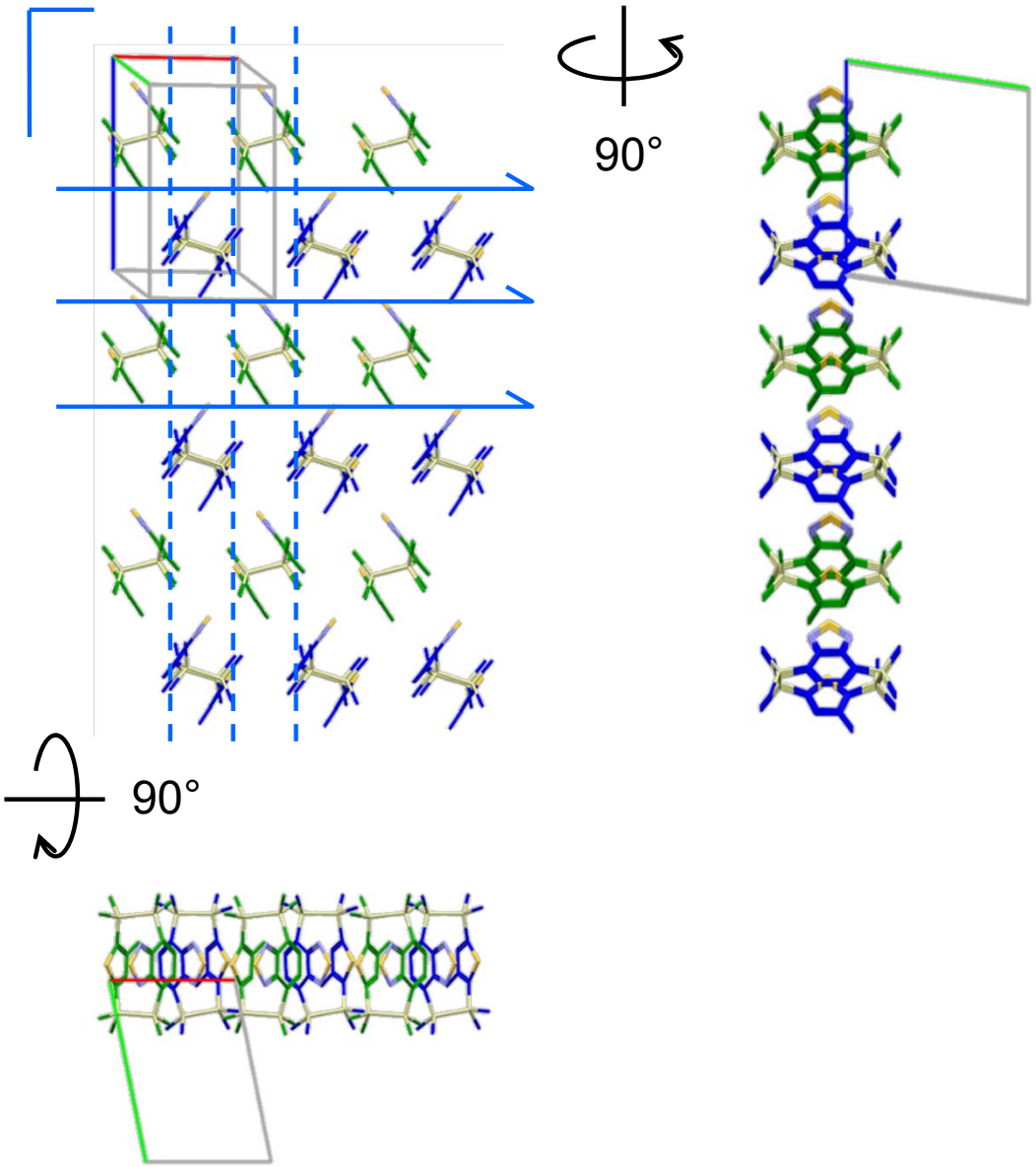
Layer (100)

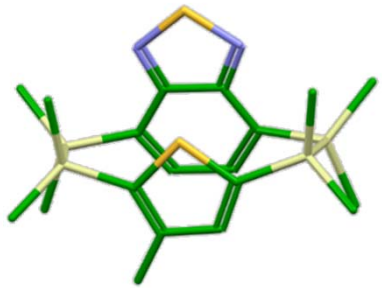


*pb*2$_1$*m*, *z'*=½ mimic, 2-D

QEFRAX
(*P*1, *Z*=2)

Layer (010)





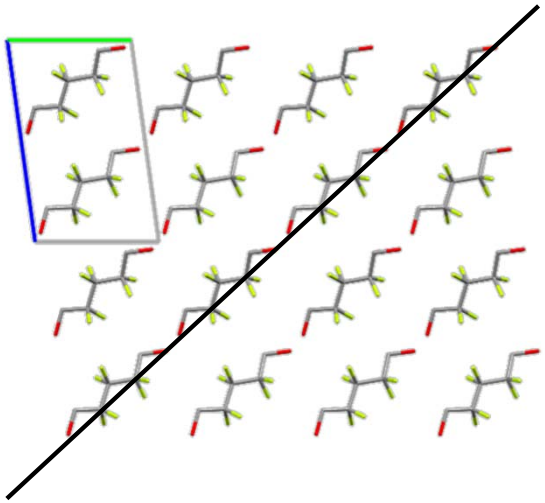
Layer (010) has very good approximate symmetry
*p*2$_1$11, *z*=2, *z'*=1
(2$_1$ along **a**; angle 88.9°)
If the unmatched Me group is ignored the approximate symmetry is *p*2$_1$*am* (standard setting *pb*2$_1$*m*), *z'*=½, with the molecule lying on the mirror plane

distorted *pba*2, 2-D

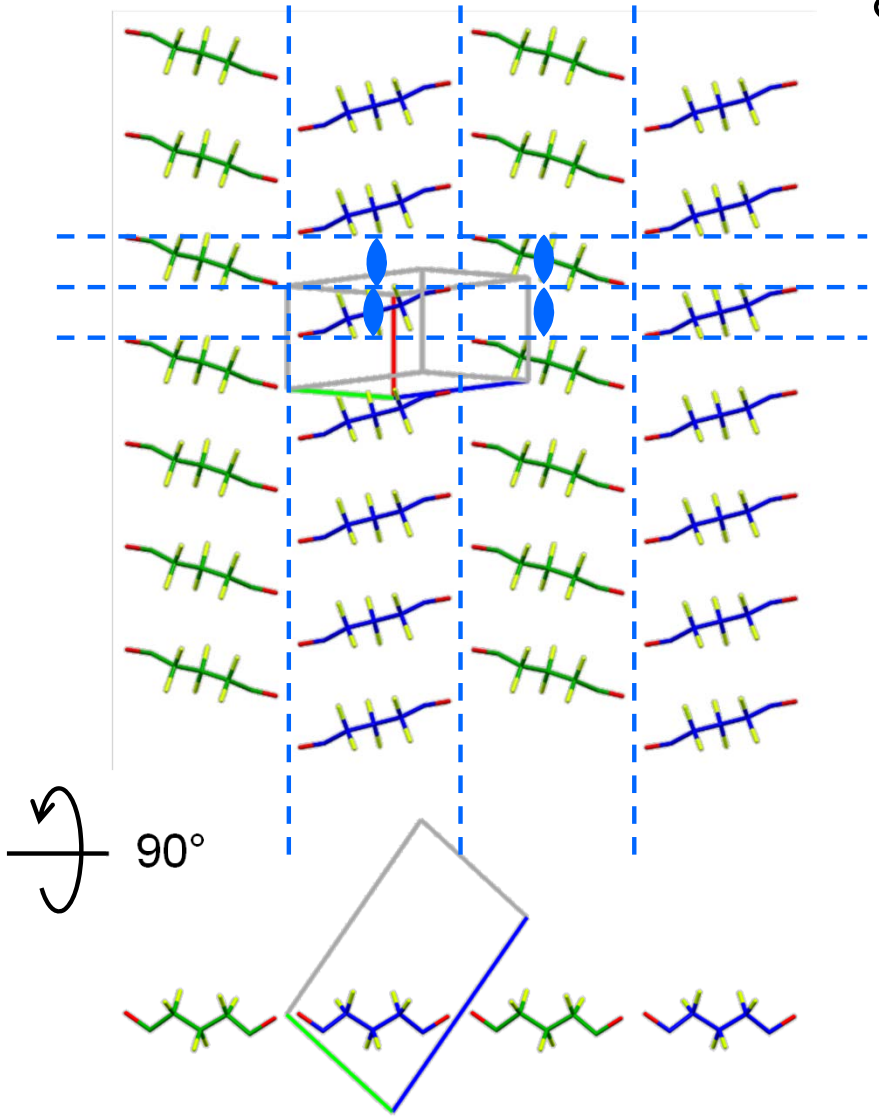
QUBPIN
(*P*1, *Z*=2)

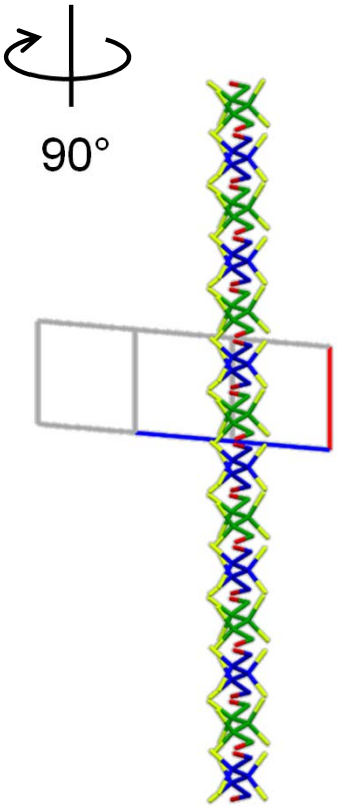
View along a

Layer (012)



(012)





Layer (012)
*pba*2 , *z*=2, *z'*=½
axes [100], [02$\bar{1}$],
angle 90.0°

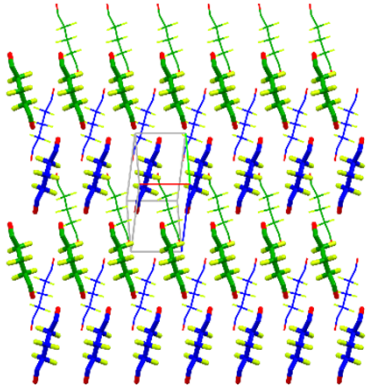
(see also next page)

The “polymorphs” Ic, Ia, and Ib are very similar;
in polymorph II (QUBPIN02) the layer offset is slightly different

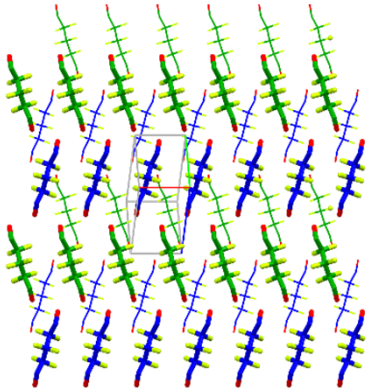
QUBPIN, con’t
(*P*1, *Z*=2)

Views along (012)

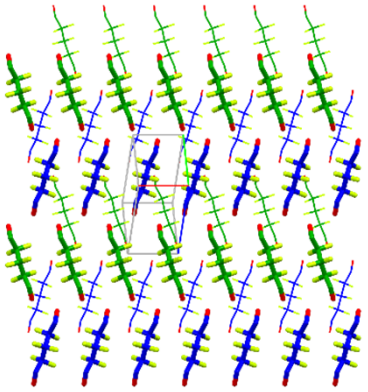
QUBPIN (283 K)



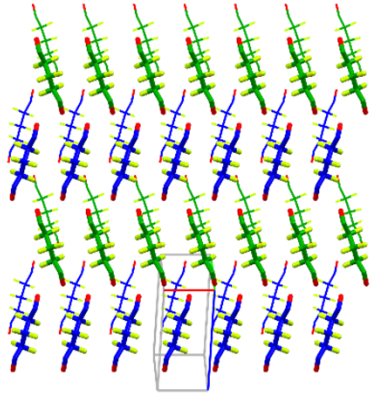
QUBPIN03 (283 K)

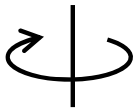


QUBPIN01 (173 K)
(metastable)

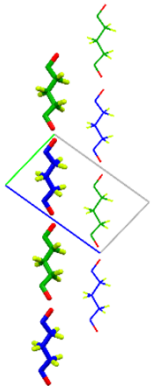


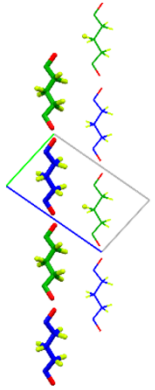
QUBPIN02 (173 K)

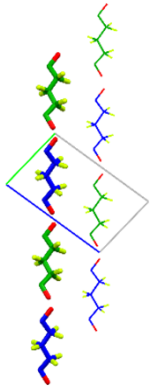




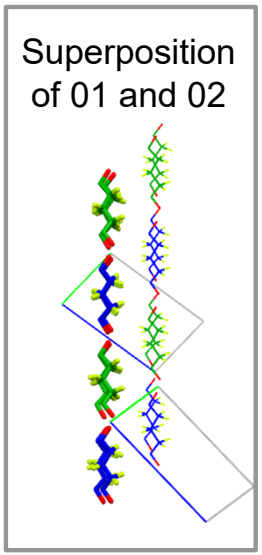
90°

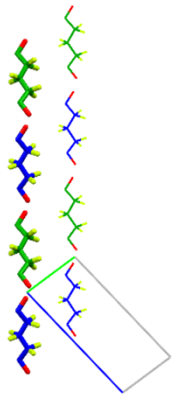






Superposition
of 01 and 02

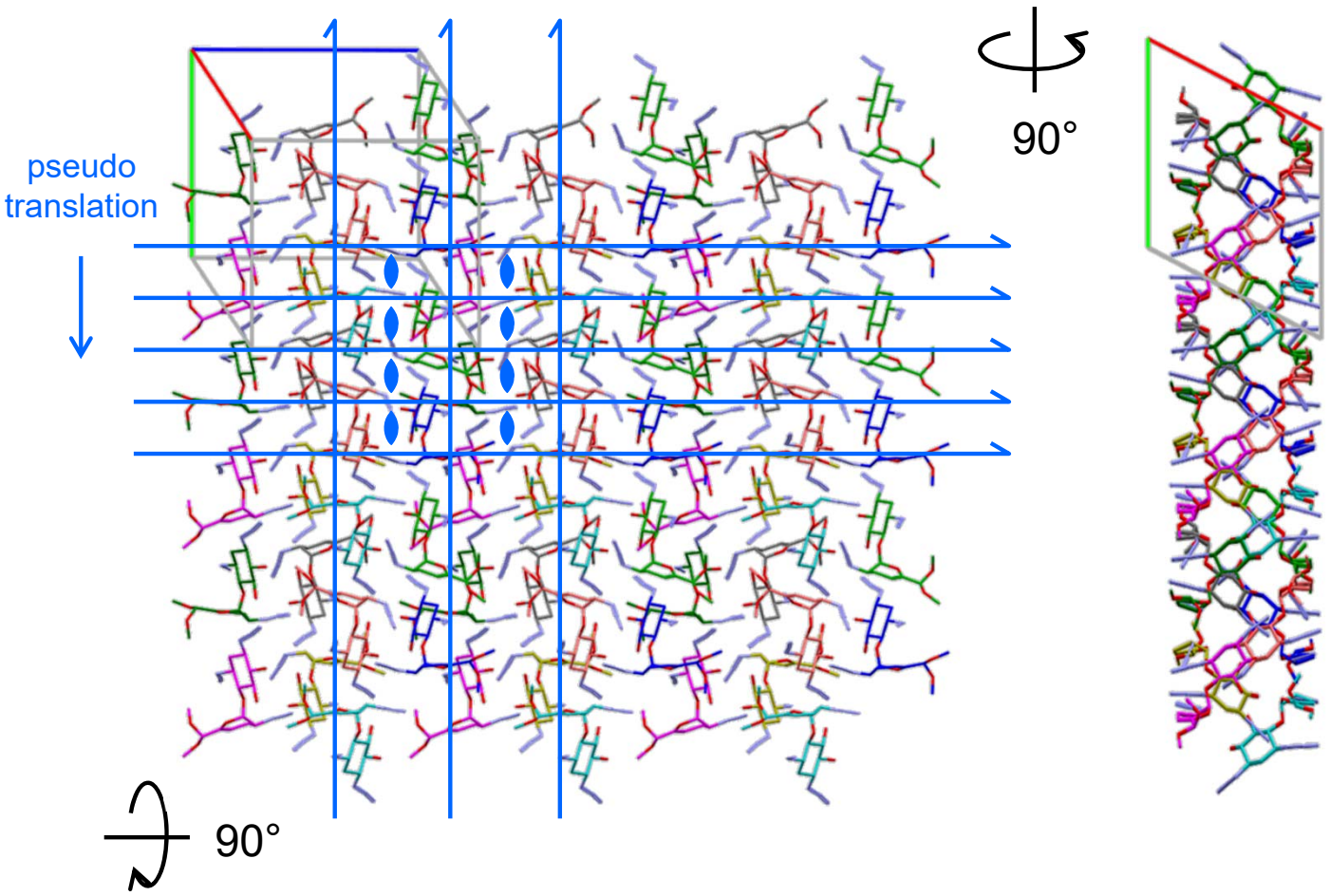


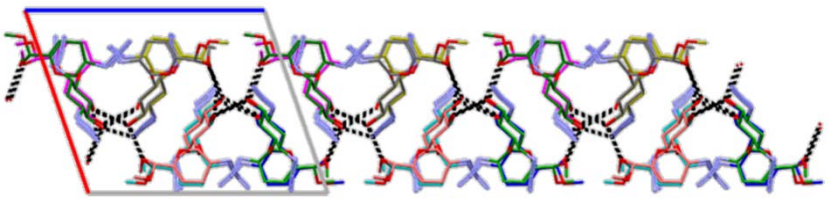


distorted $p2_12_12$, with an approximate translation (**b'**=**b**/2), 2-D

RAKBUC
(*P*1, *Z*=8)

Layer (100)





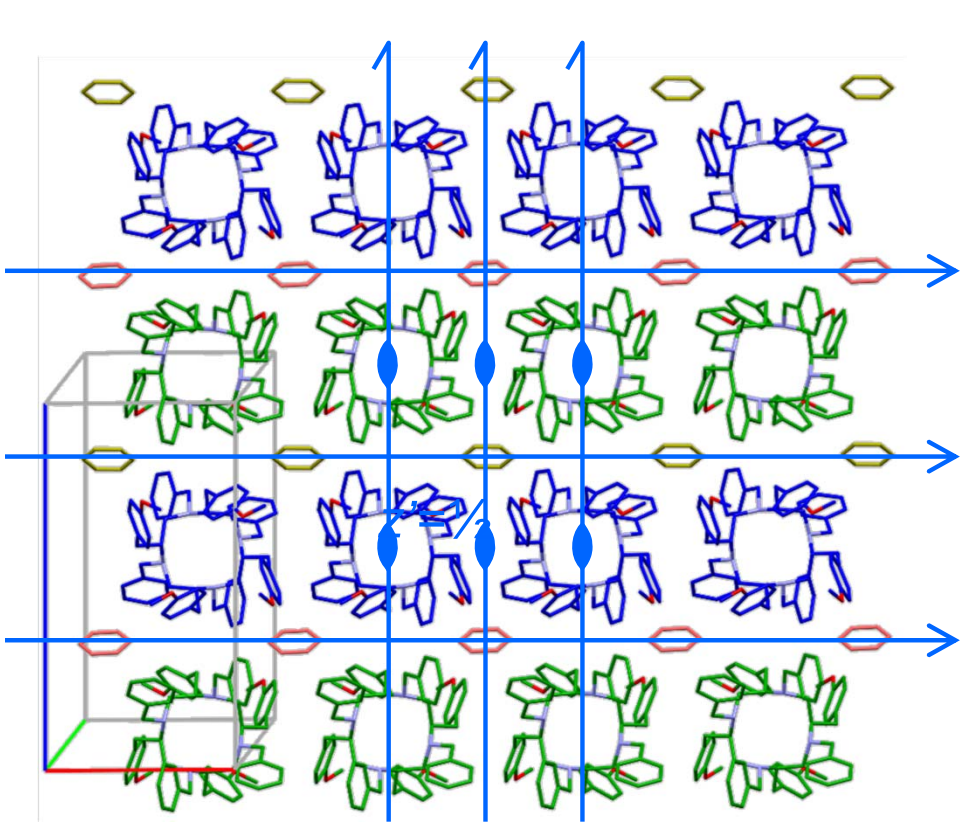
(H bonds shown
in this view only)

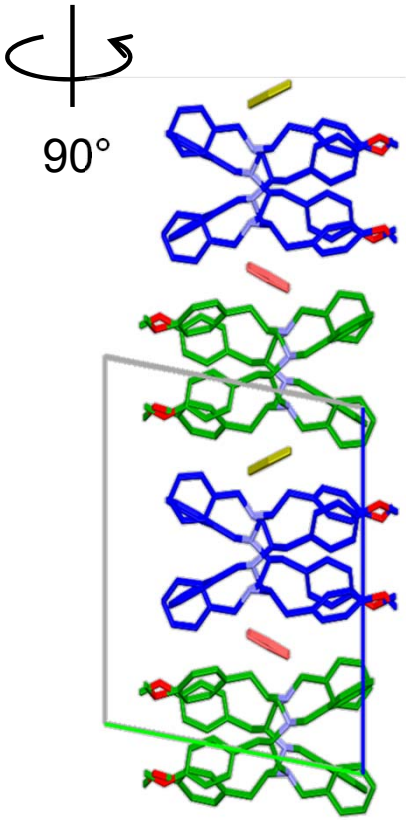
Layer (100)
$p2_12_12$, z=4, z'=1
axes [010]/2, [001],
angle 89.7°

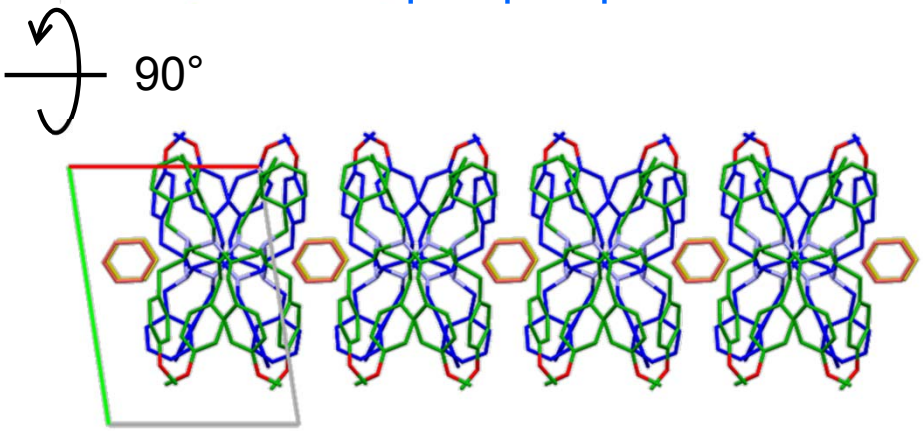
distorted $p2_122$, $z'=½$, 2-D

UJADOZ
($P1$, $Z=2$)

Layer (100)





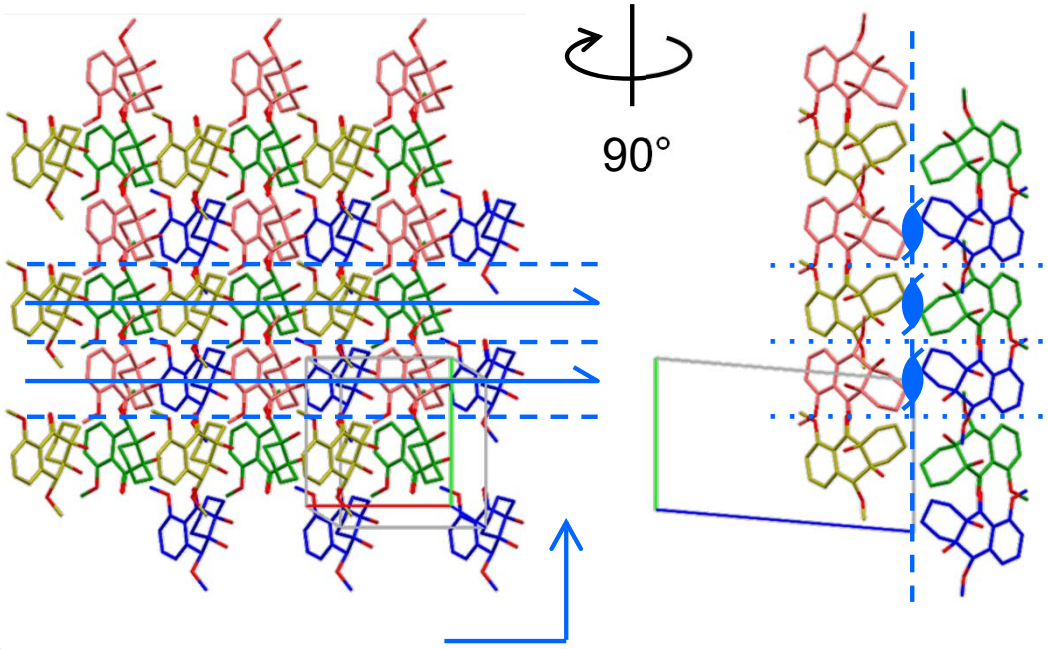


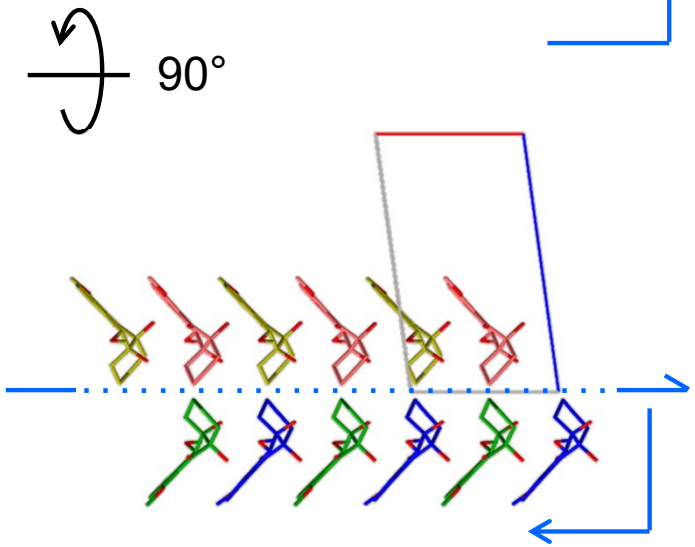
Layer (010)
$p2_122$, $z=2$, $z'=½$
axes [001], [100],
angle 89.6°

distorted $pb2_1a$, 2-D (a kryptoracemate)

VEHDEU
($P1$, Z=4)

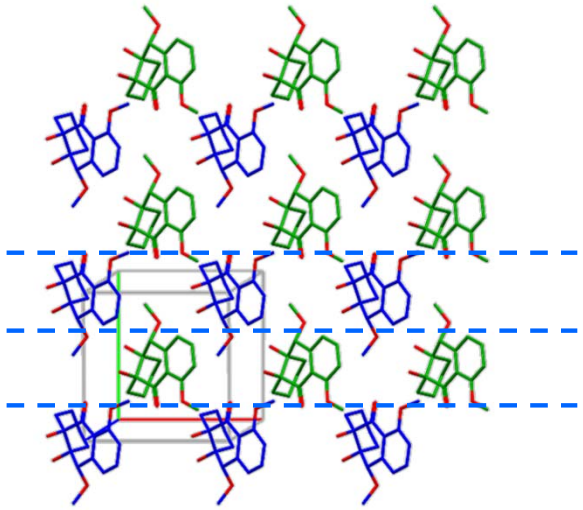
Layer (001)

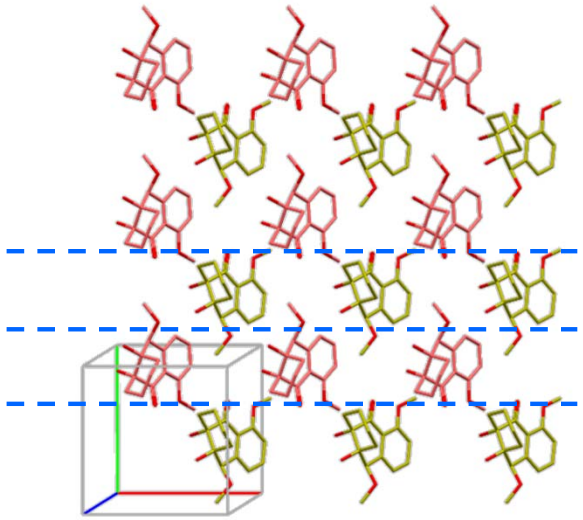




Layer (001)
$pb2_1a$, z=4, z`=1
axes [110], [1$\bar{1}$0],
angle 90.1°

Parts of layer (001)



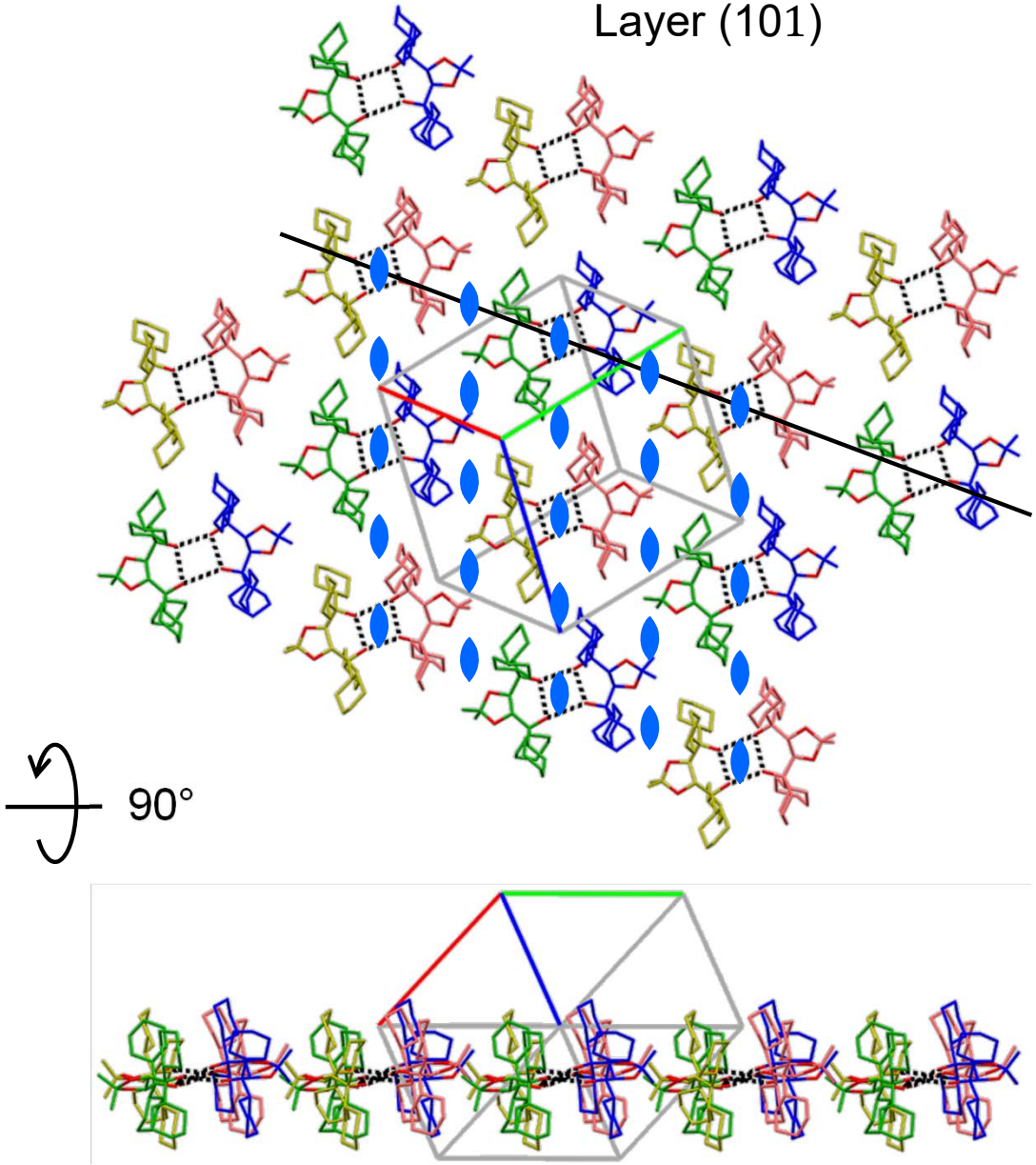


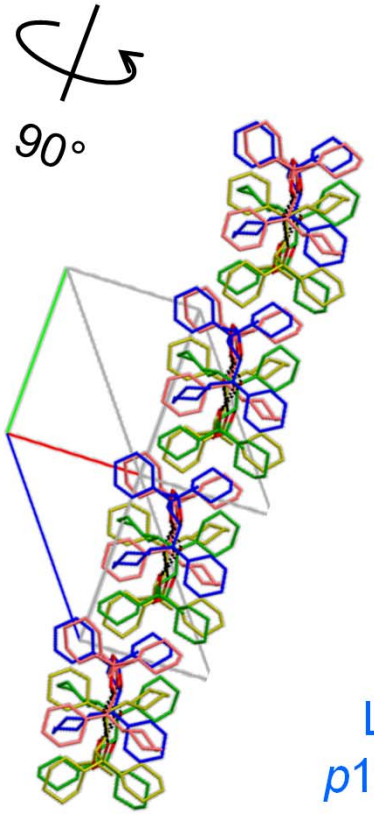
distorted *p*112 with an approximate translation (**a**'=[11$\bar{1}$]/2, **b**'=[$\bar{1}$11]/2), 2-D

([11$\bar{1}$]/2, and [$\bar{1}$11]/2 are the same because [11$\bar{1}$]/2+[$\bar{1}$01]=[$\bar{1}$11]/2)

YONVOM (*P*1, *Z*=4)

Layer (10$\bar{1}$)





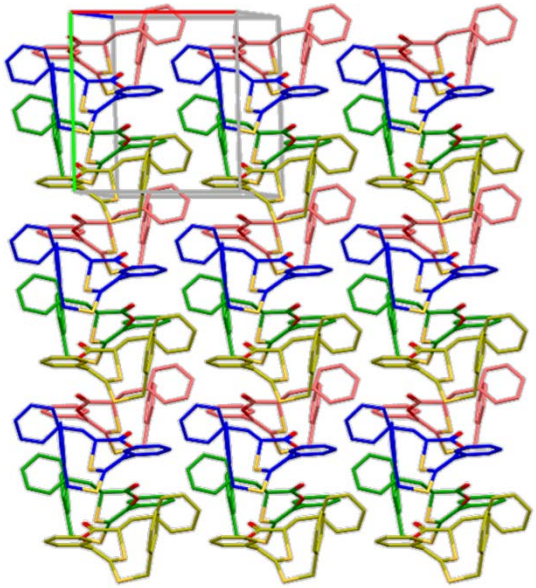
Layer (10$\bar{1}$)
*p*112, *z*=2, *z'*=1
axes [11$\bar{1}$]/2, [$\bar{1}$11]/2
although the twofold axes are not quite parallel to the layer normal

Structures that have two kinds of layers
that alternate

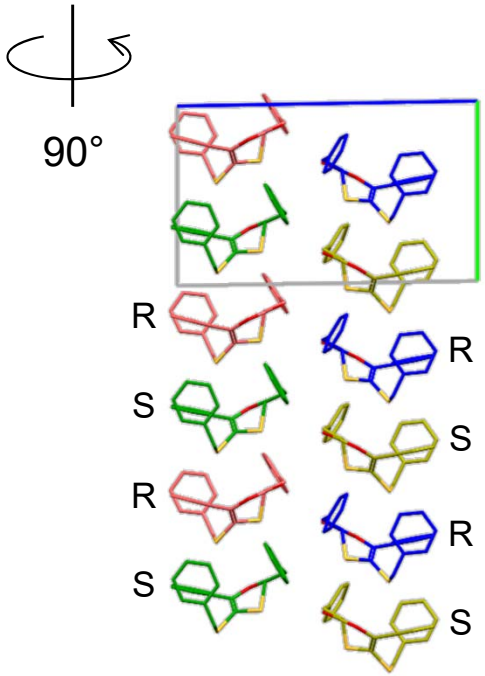
alt layers, 2-D; distorted glide (*pb*11) (a kryptoracemate)

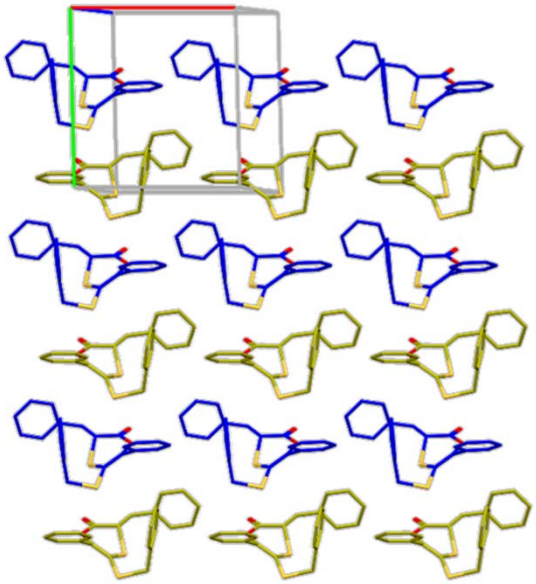
CEHYEW
(*P*1, *Z*=4)

View of two layers (001)

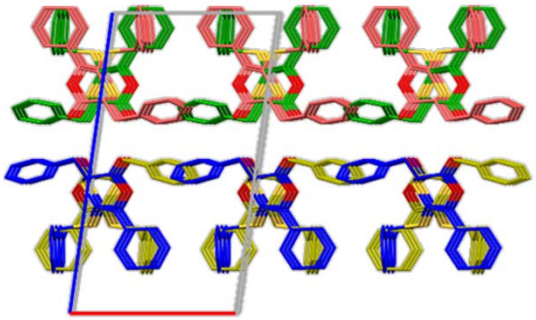


90°

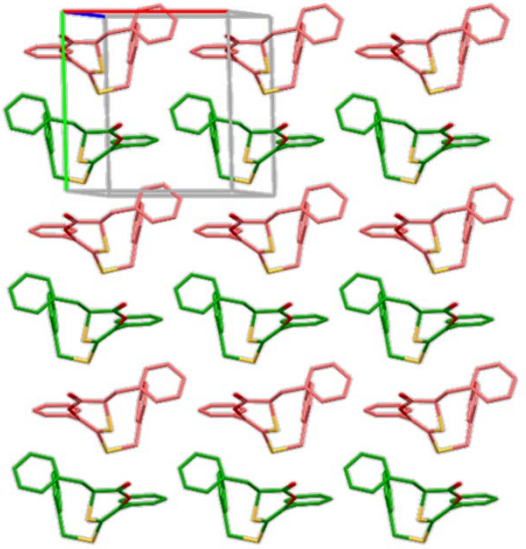




90°



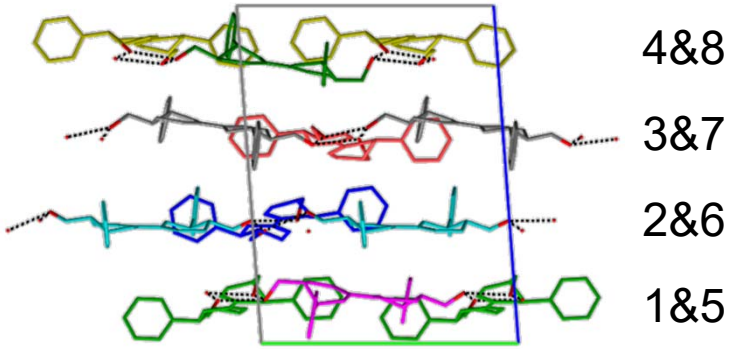
Two layers (001)
*pb*11, *z*=2, *z'*=1
axes [100], [010]
(because of the offset the two layers are not related by any approximate periodic symmetry)



alt layers, 2-D

View along **a**

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

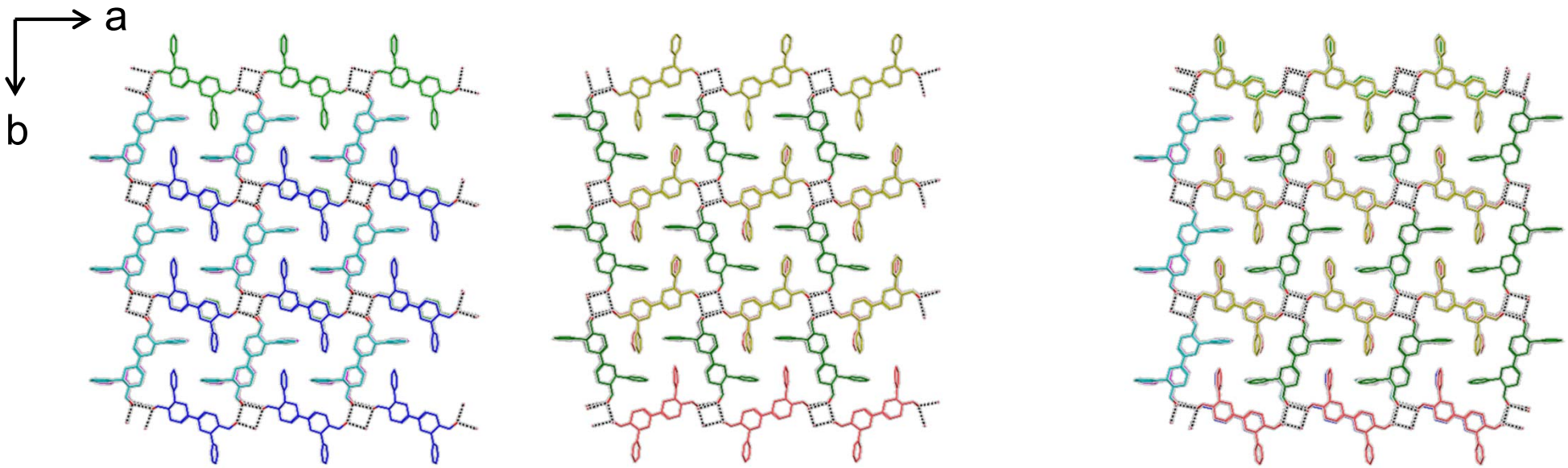


Layers (001)

Superposition by translation of 1&5 and 2&6

Superposition by translation of 3&7 and 4&8

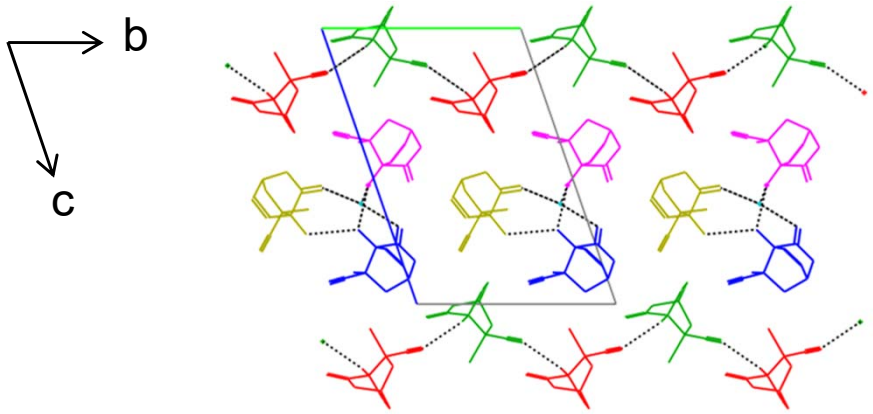
Superposition of all four after rotation of 3&7 and 4&8 by 180° around **b**



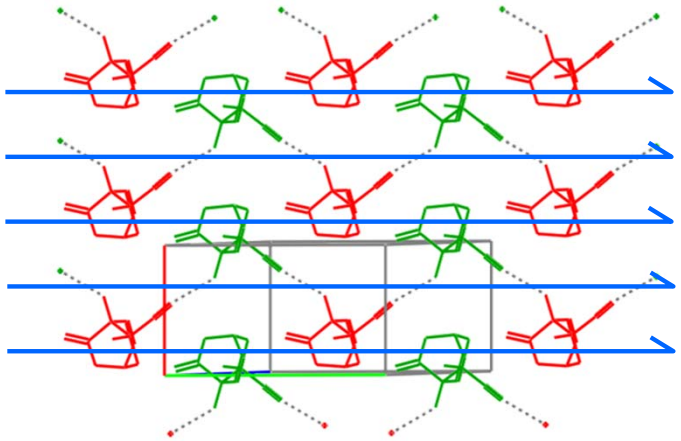
alt layers, 2-D

CIFGEE
(*P*1, *Z*=5)

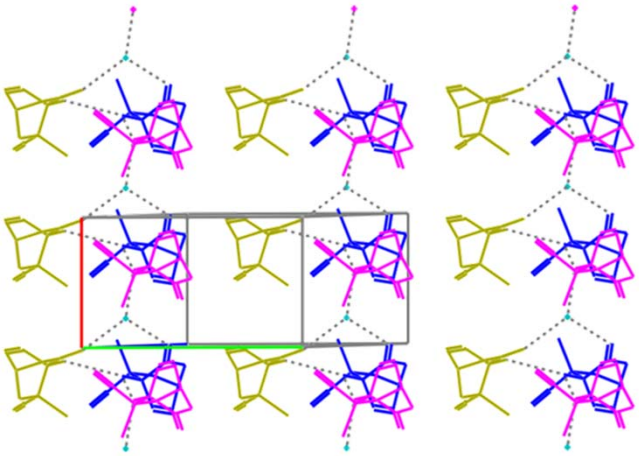
View along **a**



Layers (001)



$p2_111$, z=2, z'=1
axes [100], [010]

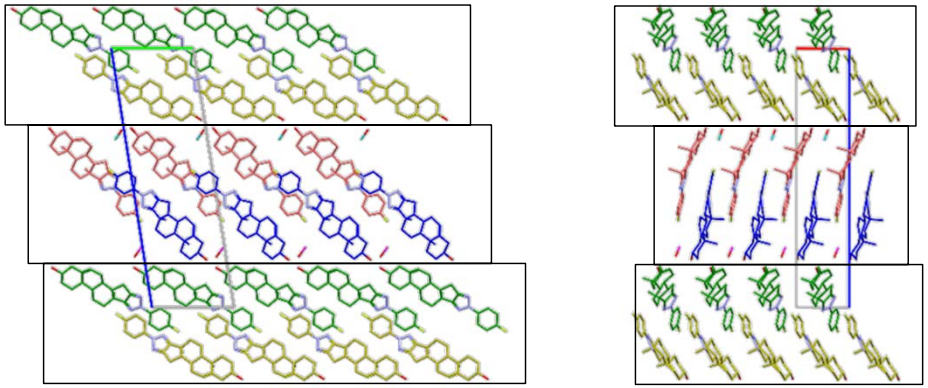


$p1$, z=1, z'=1

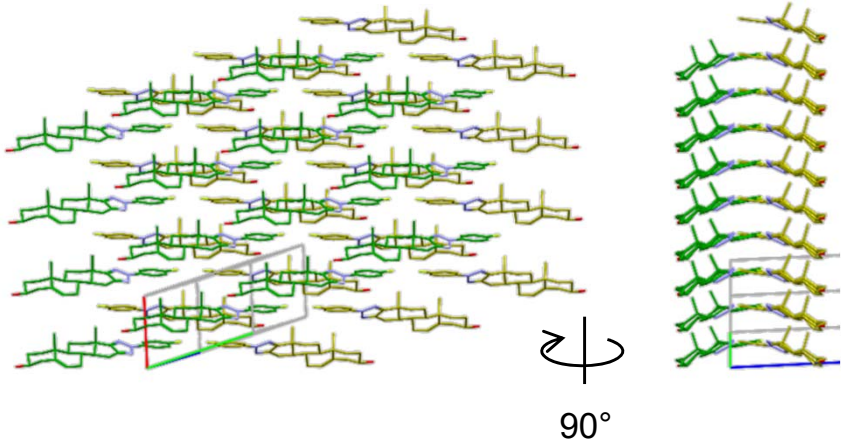
alt layers, 2-D

Views along **a** and **b**

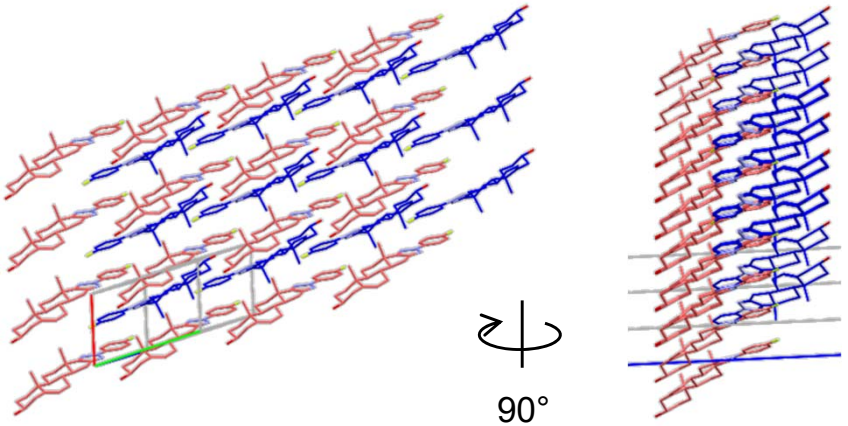
EVOREM
(*P*1, *Z*=4)



Views along **c*** and **b** of layers (001)



*c*211, *z*=4, *z'*=1
axes [100], [$\bar{1}$20]

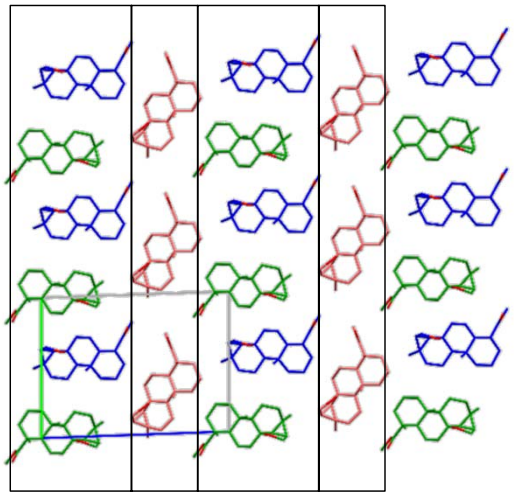


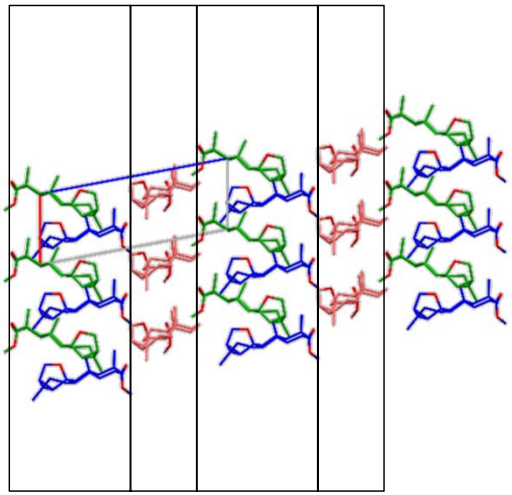
p$\bar{1}$, *z*=2, *z'*=1

alt layers, 2-D

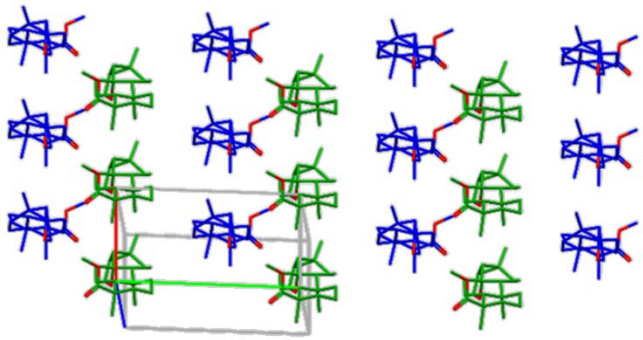
Views along **a** and **b**

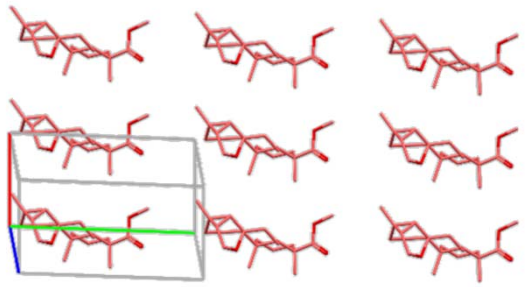
FUXYUS
(*P*1, *Z*=3)





Layers (001)





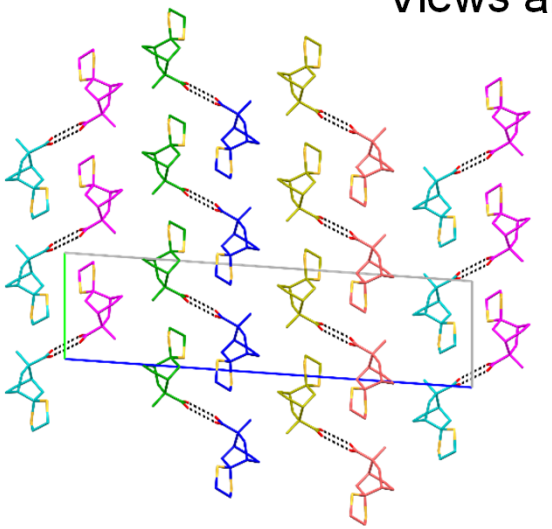
$p2_111$, z=2, z'=1
axes [100], [010], angle 92.0°

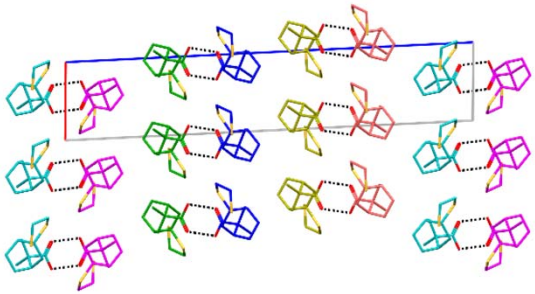
$p1$, z=1, z'=1

alt layers, 2-D

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

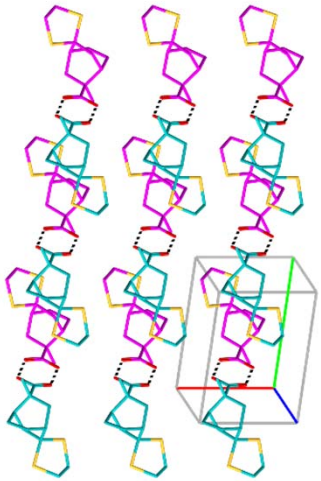
Views along **a** and **b**

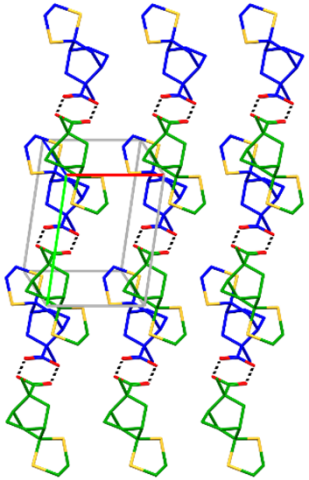


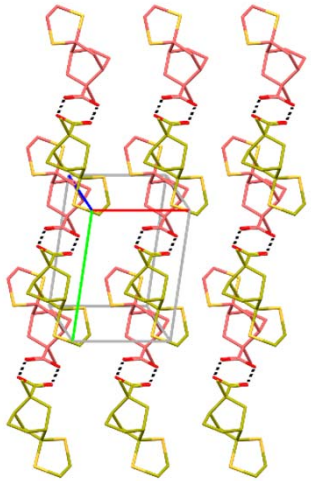


Layers of #1&2 and of #3&4 are related by local translation;
#1&2 is related to #5&6 by a local glide;
the relationship of #3&4 and #5&6 is a local 2_1 along **c***

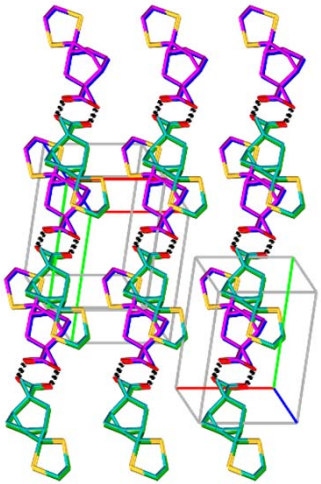
Layers (001) and their superposition with translation and rotation







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

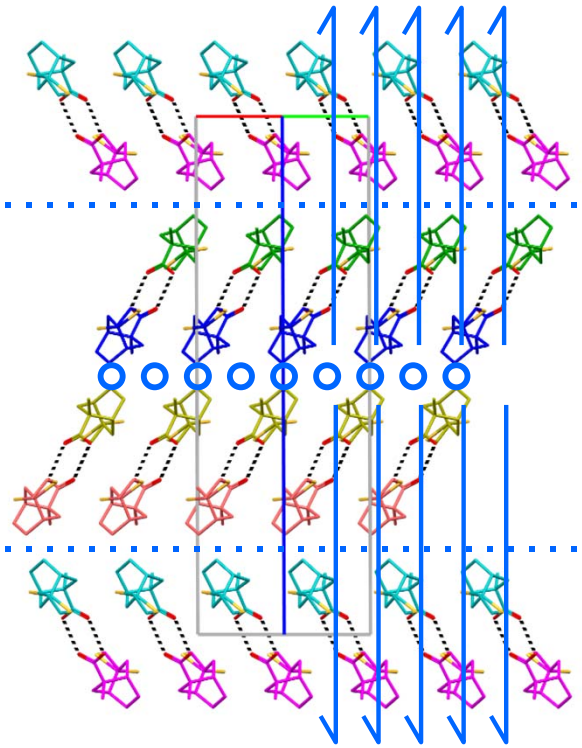


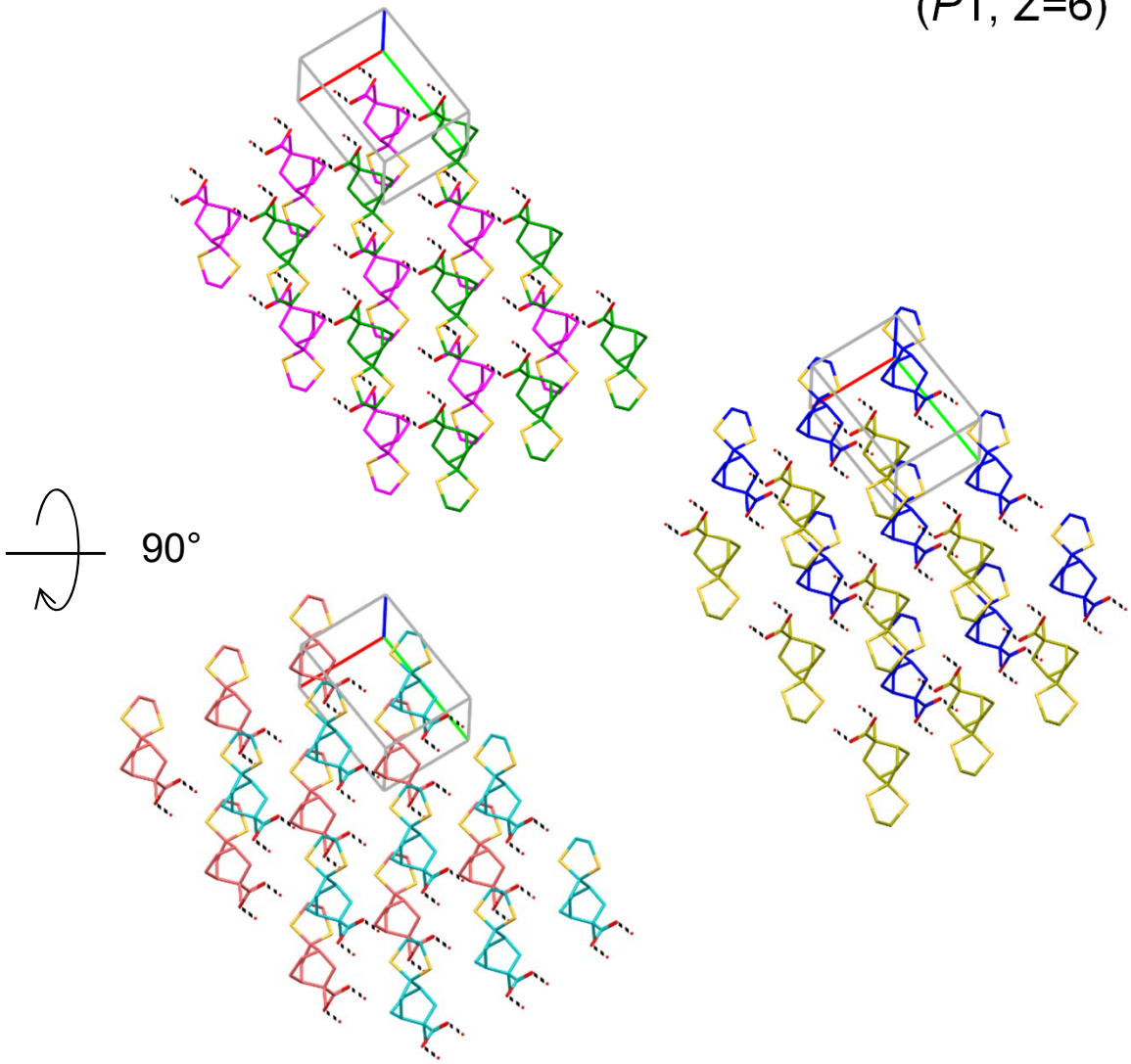
(see also next page)

alt layers, 2-D

GIPLID,
con't
(*P*1, *Z*=6)

View along [110]



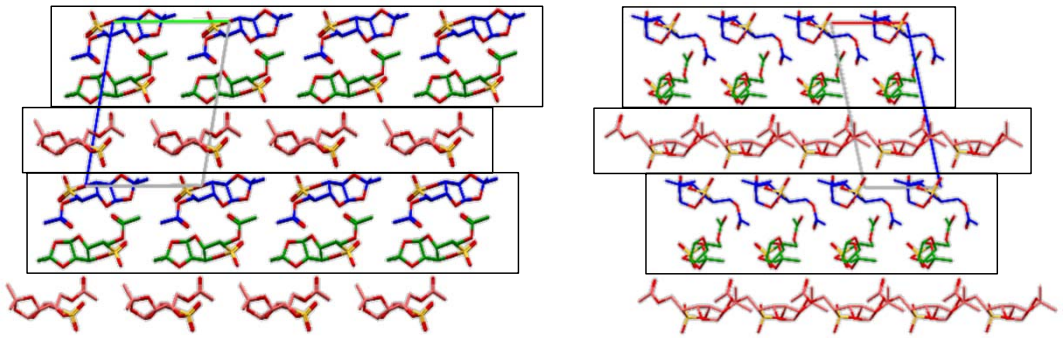


All of the approximate
symmetry is local only

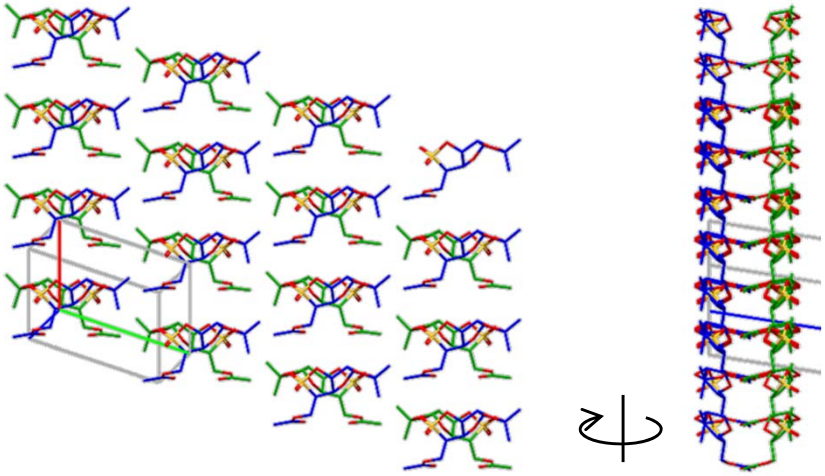
alt layers, 2-D

Views along **a** and **b**

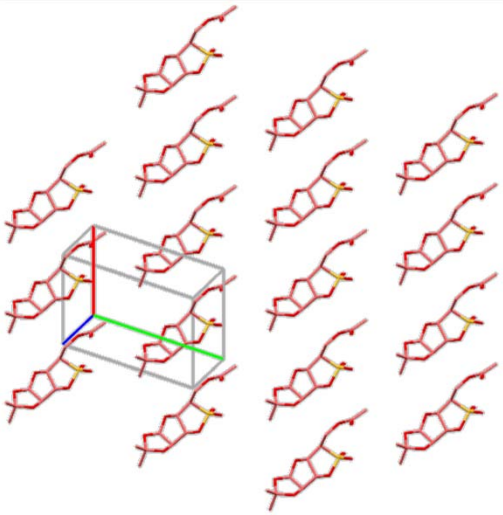
GUVROF
(*P*1, *Z*=3)



Layers (001)



*c*211, *z*=4, *z'*=1
axes [100], [120]

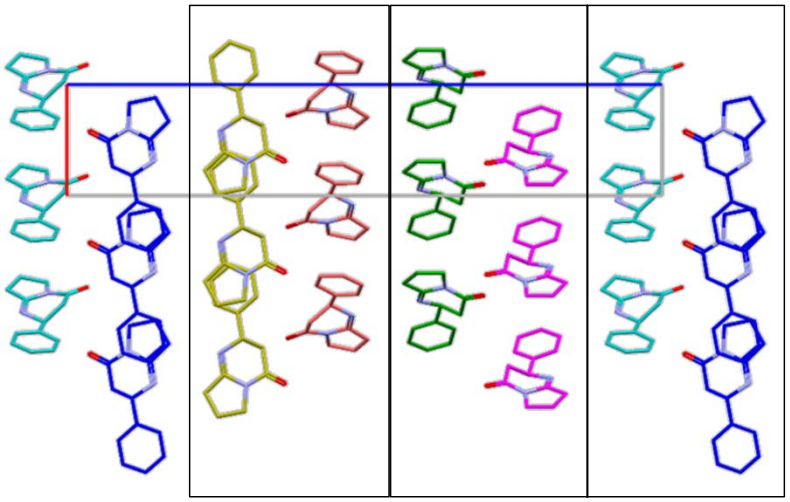


*p*1, *z*=1, *z'*=1

alt layers, 2-D

View along **b**

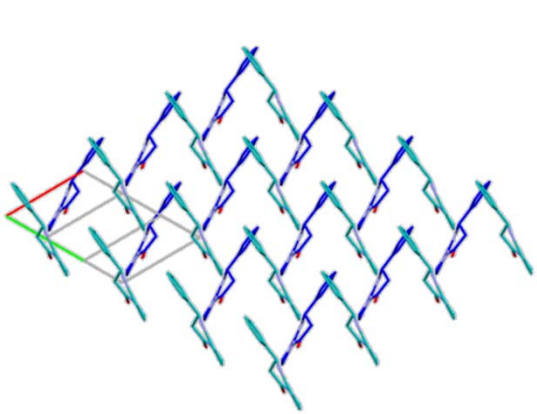
cell constants:
7.33, 7.34, 34.14 Å
83.8, 86.9, 60.2°

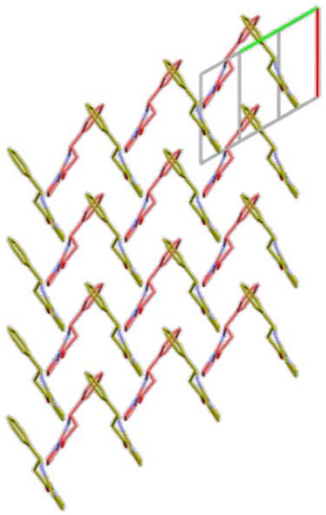


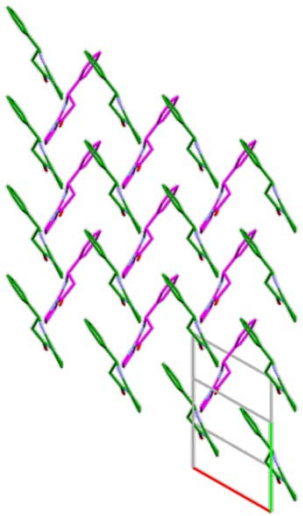
HINKUN
(*P*1, *Z*=6)

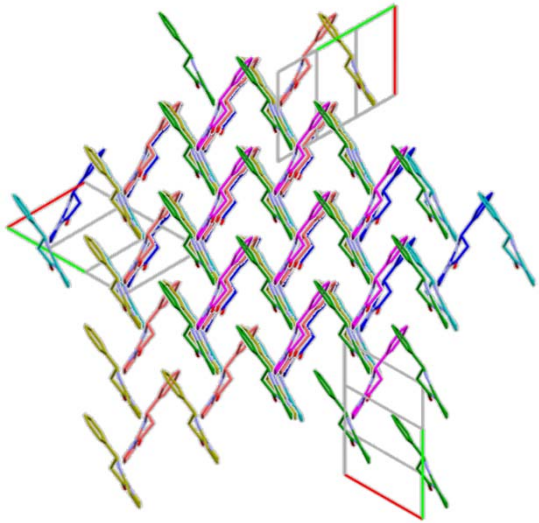
Bilayers (001) *c*211, *z*=4, *z'*=1 are related by approximate 3_1 axes but the positions of those axes vary

Bilayers (001) and their superposition by translation





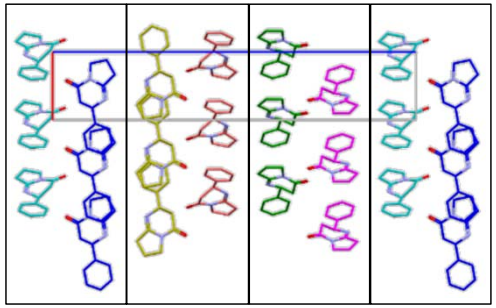




(see also next page)

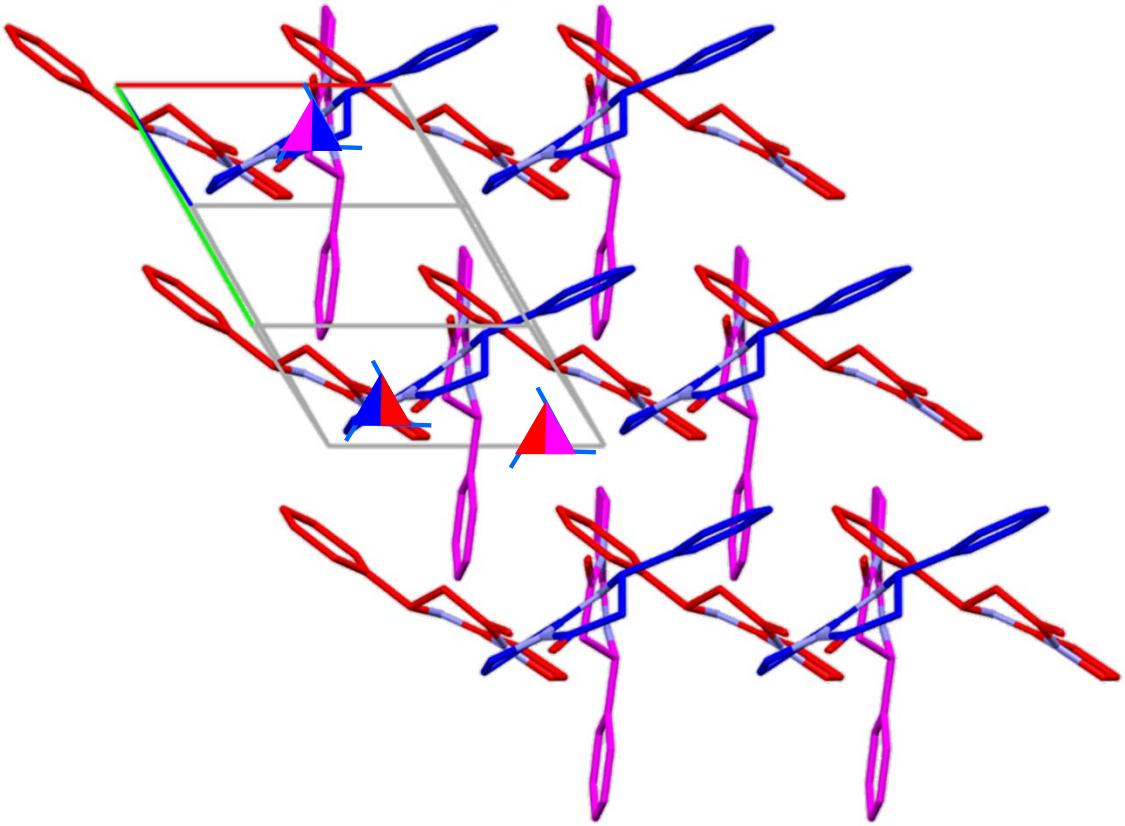
alt layers, 2-D

View along **b**



HINKUN, con't (*P*1, *Z*=6)

View along **c*** of molecules #2, 3, and 5

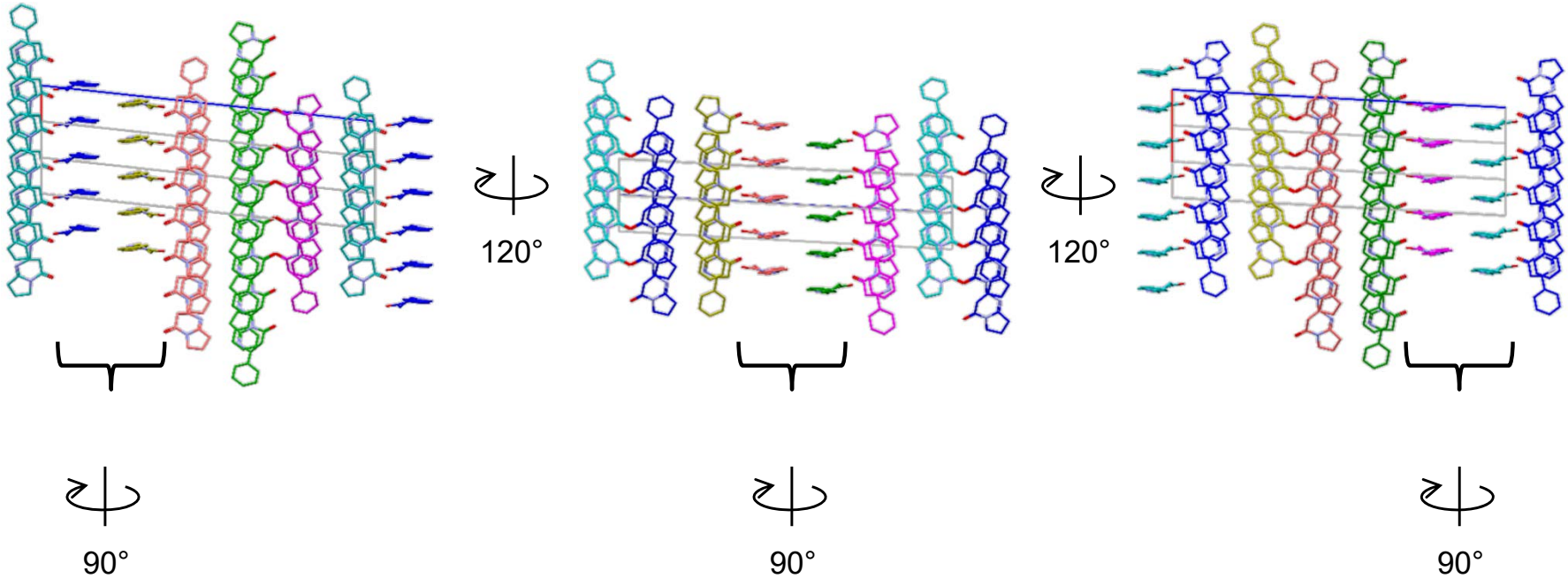


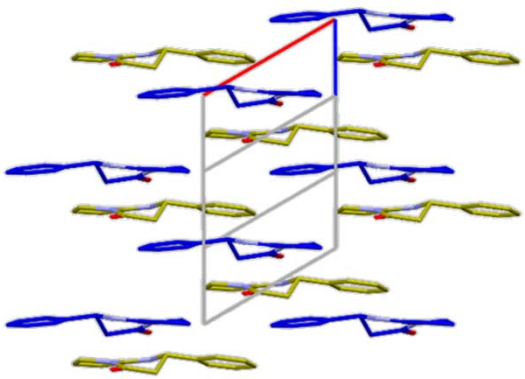
Positions of the approximate 3_1 axes vary

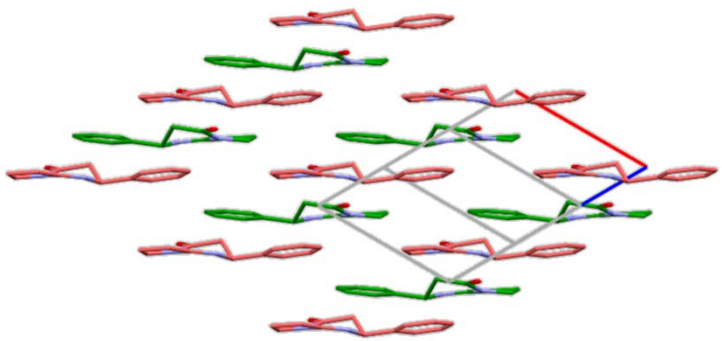
(see also next page)

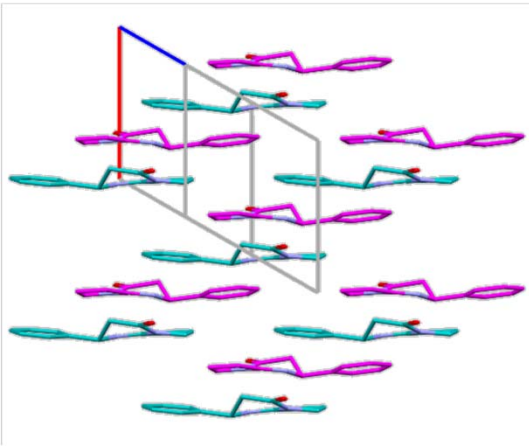
It seems as if adjacent bilayers might be related by approximate 2_1 axes, but those axes are local only

HINKUN, yet again (*P*1, *Z*=6)





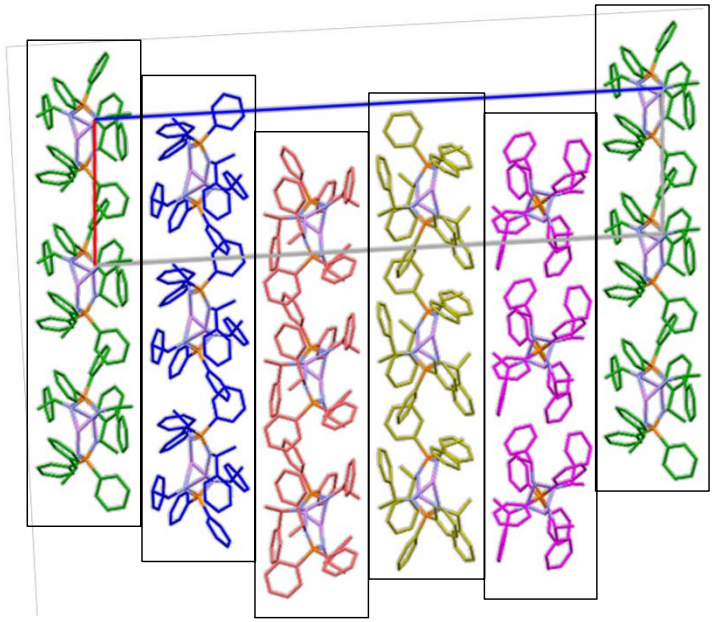




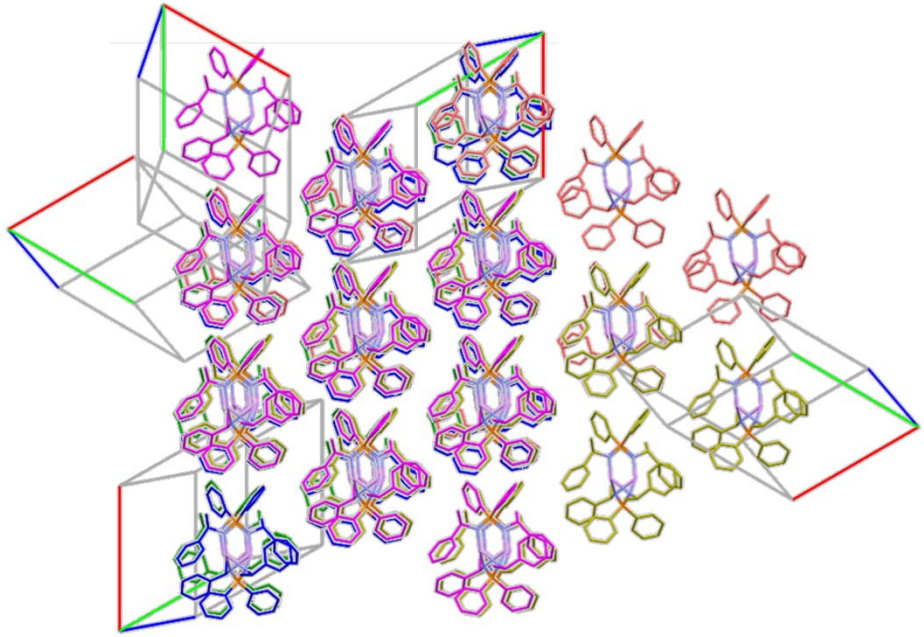
alt layers, 2-D

HOCYEG
(*P*1, *Z*=5)

View along **b**



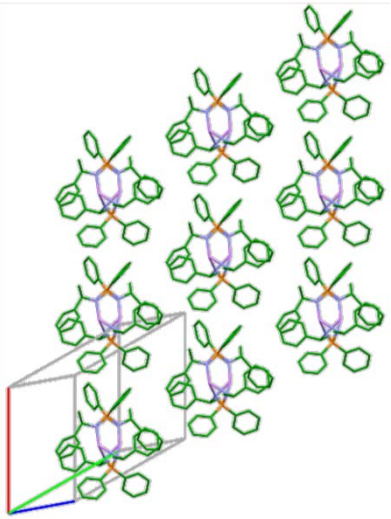
Layers (001)
superimposed
by rotation and
translation



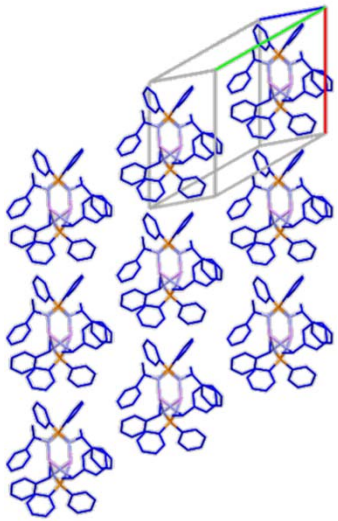
Layers (001)
*c*211, *z*=2, *z'*=½

(see also next page)

alt layers, 2-D

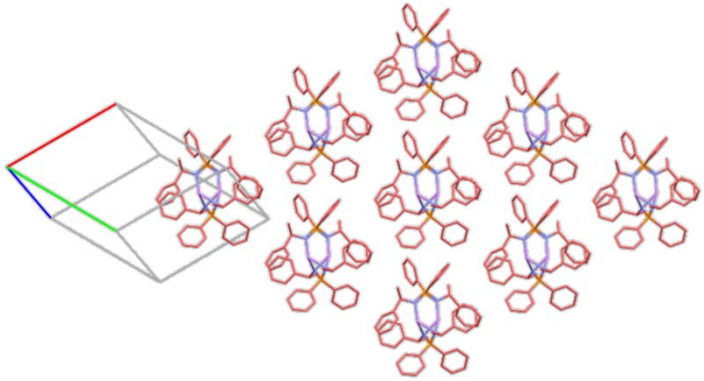


axes [100], [$\bar{1}$20]

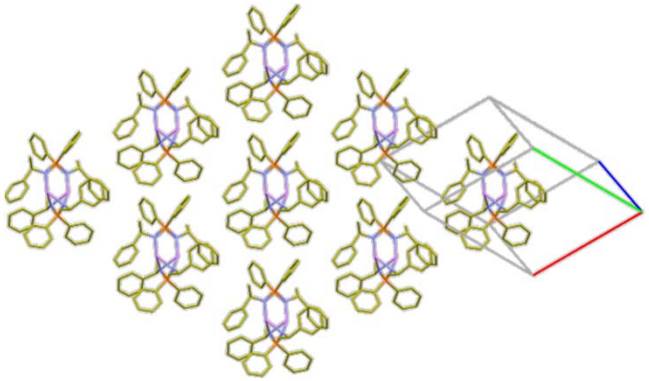


axes [$\bar{1}$00], [1$\bar{2}$0]

Layers (001)
*c*211, *z*=2, *z'*=½

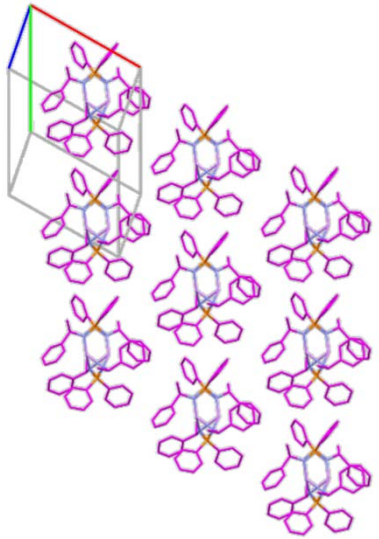


axes [1$\bar{1}$0], [110]



axes [$\bar{1}$10], [$\bar{1}\bar{1}$0]

HOCYEG,
con't
(*P*1, *Z*=5)

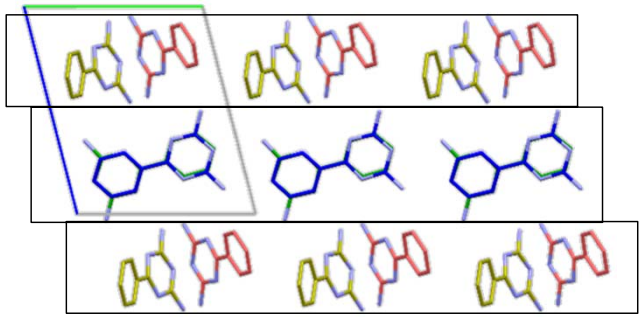


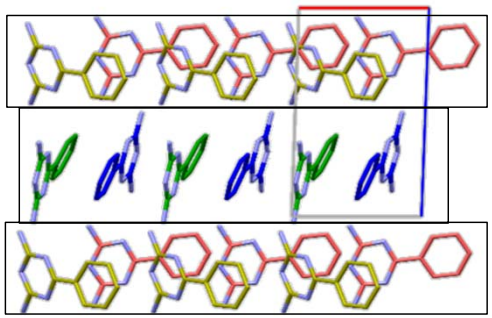
axes [0$\bar{1}$0], [2$\bar{1}$0]

alt layers, 2-D

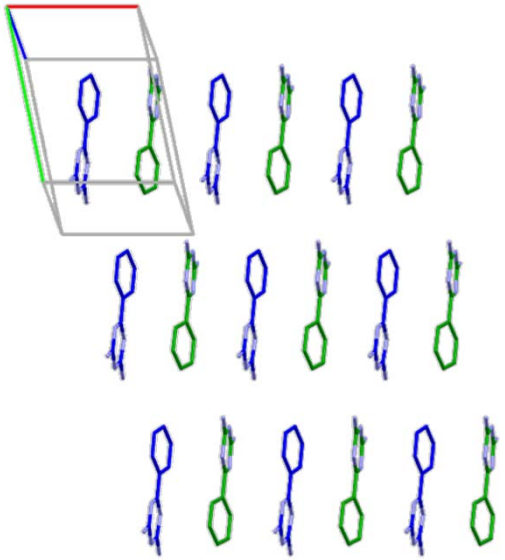
Views along **a** and **b**

IBIJAF01
(*P*1, *Z*=4)

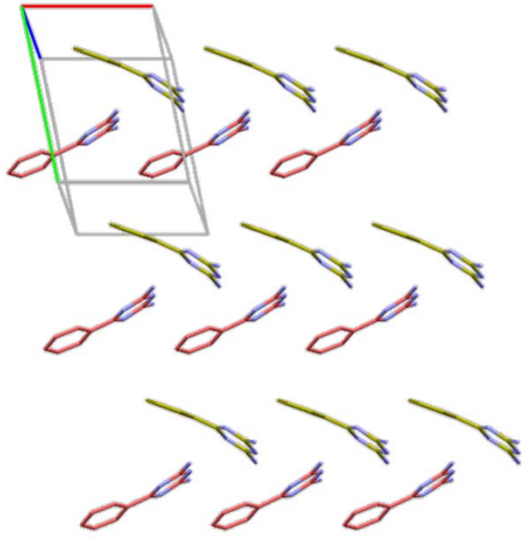




Layers (001)



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

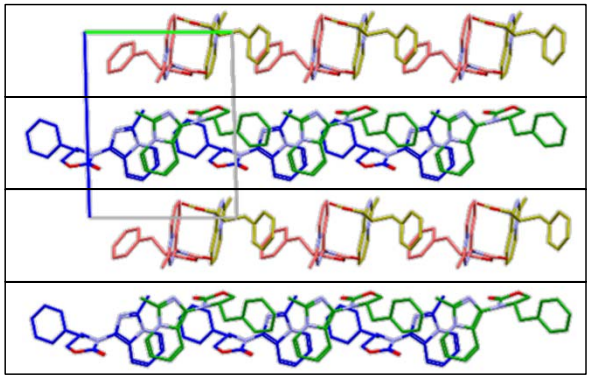


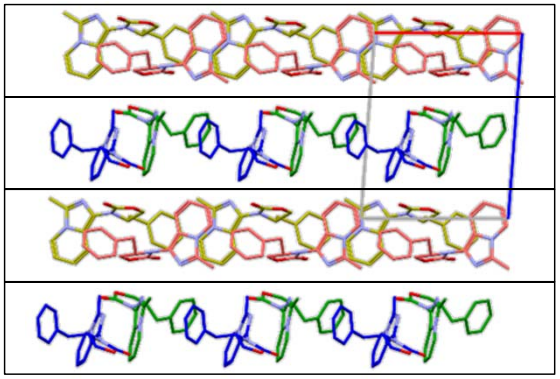
2_1 axes but 1-D only
(γ = 78.3°)

alt layers, 2-D

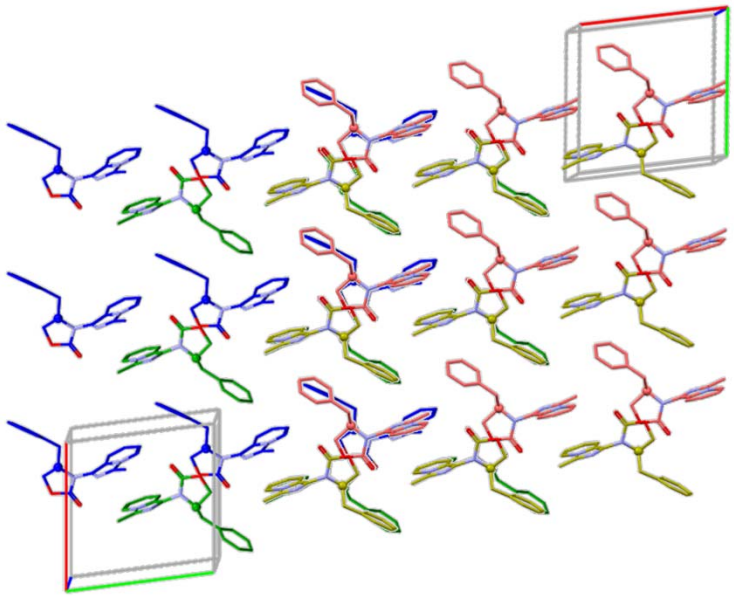
Views along **a** and **b**

QACXUN
(*P*1, *Z*=4)





Superposition of layers (001)



Layers look like $p\bar{1}$ mimics (z=2, z'=1) having different orientations but the layer of #1&2 has hybrid packing

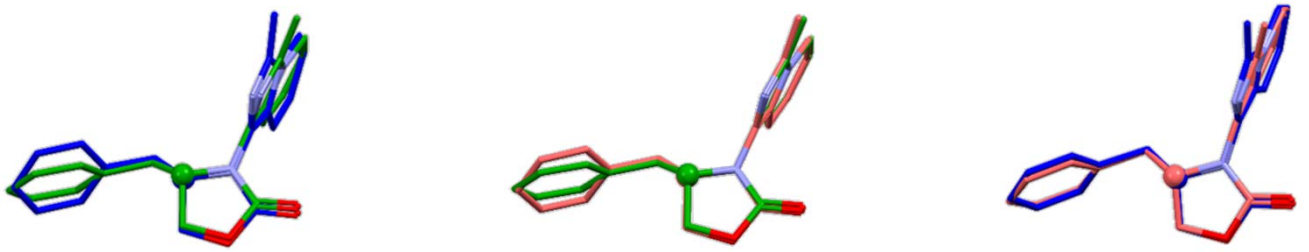
(see also next page)

alt layers, 2-D

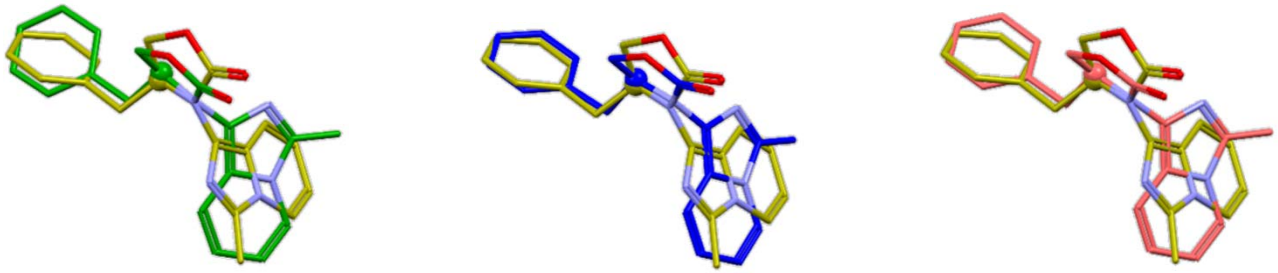
QACXUN, con't
(*P*1, *Z*=4)

Molecules #1, 2, 3 have the same conformation; molecule #4 is their approximate enantiomer

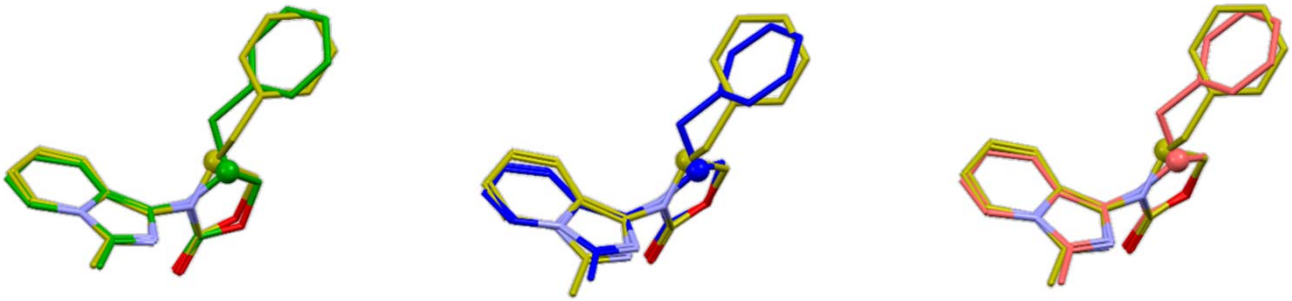
pairwise overlays of #1, 2, 3



pairwise overlays of #1, 2, 3 with #4



pairwise overlays of inverted #1, 2, 3 with #4



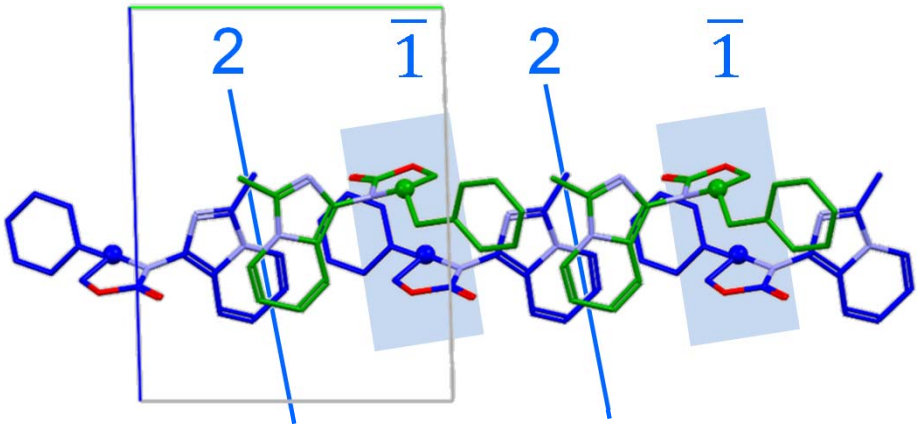
(see also next page)

alt layers, 2-D

QACXUN,
yet more
(*P*1, *Z*=4)

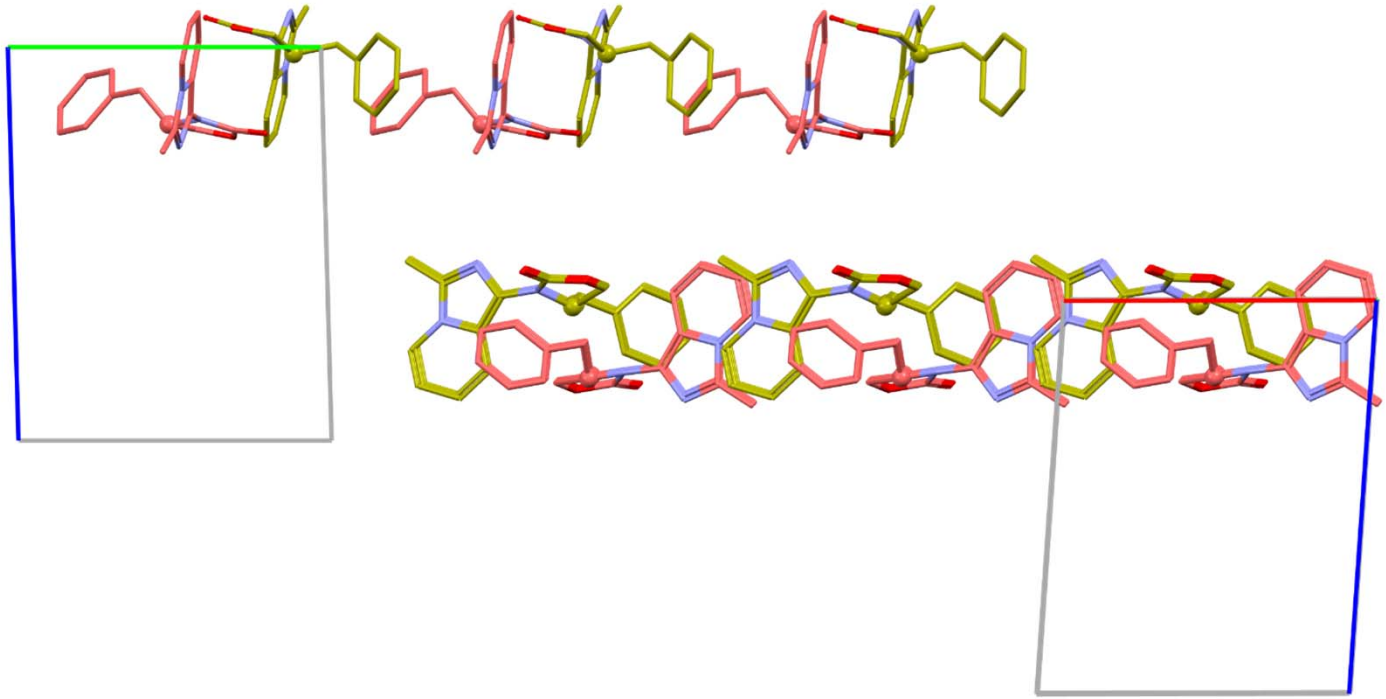
Part of the layer
of #1&2

hybrid packing



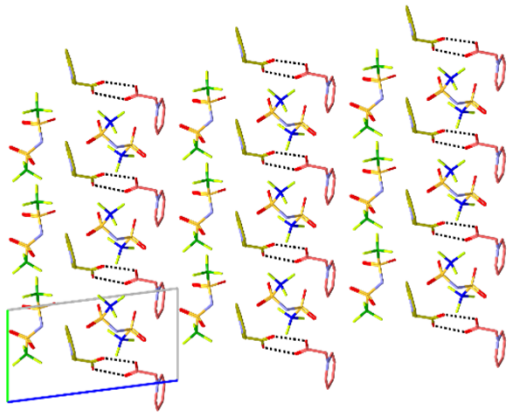
Part of the layer
of #3&4

$p\bar{1}$ mimic



alt layers, 2-D

View along **a**



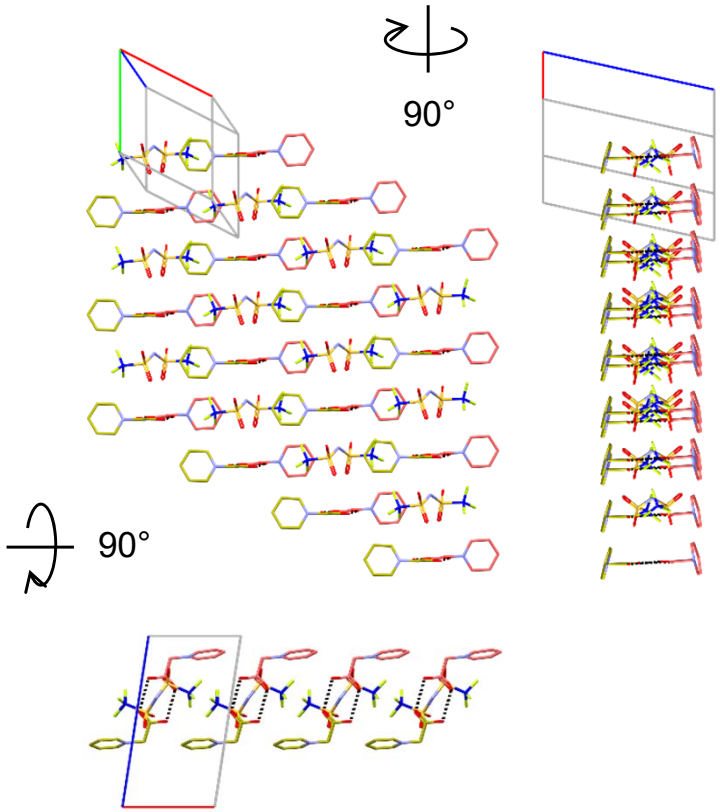
TOJRAM
(*P*1, *Z*=2)

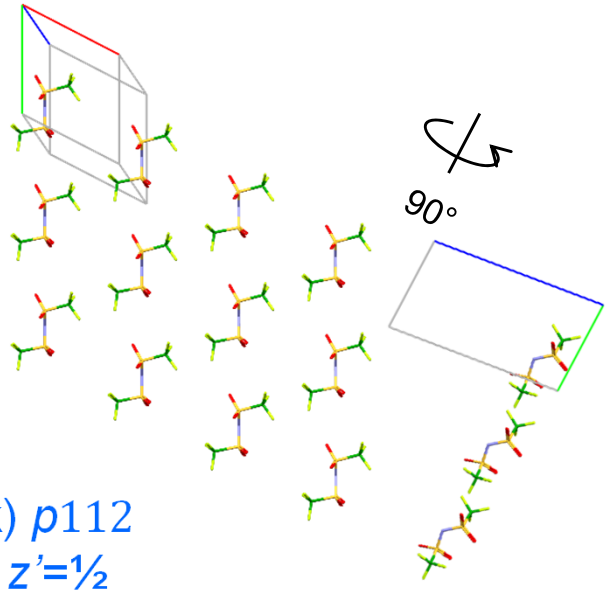
(a 1:1 salt)

*c*211, *z*=2, *z'*=1 for cation; *z*=1, *z'*=½ for the one anion

axes [010], [2$\bar{1}$0], angle 92.7°

Layers (001)





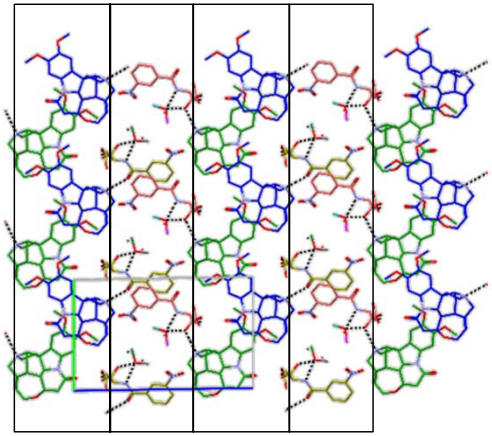
(weak) *p*112
z=1, *z'*=½
(layer of one anion)

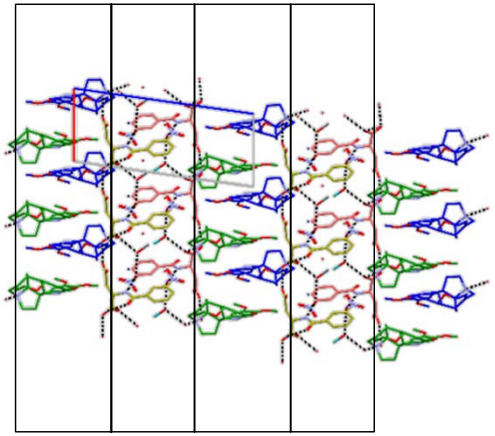
alt layers, 2-D

Views along **a** and **b**

TOLRUK
(*P*1, *Z*=2)

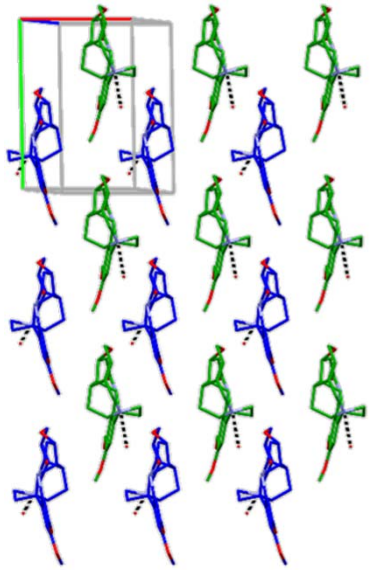
1:1:2 MeOH solvate of a brucinium salt

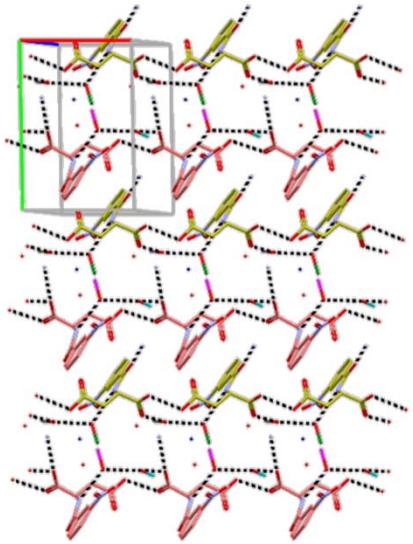




Layers (001)

$p2_111$, z=2, z'=1
axes [010], [100], angle 89.0°
(cation layer)



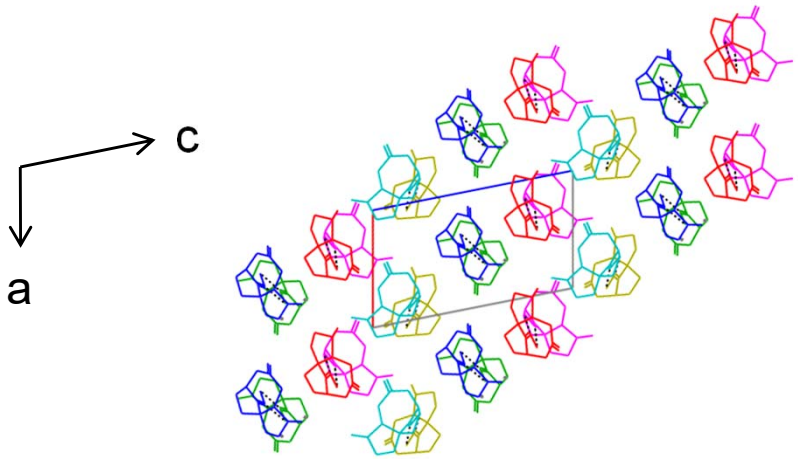


$p\bar{1}$ mimic.
z=2, z'=1
(anion, solvent layer)

alt layers, 2-D

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

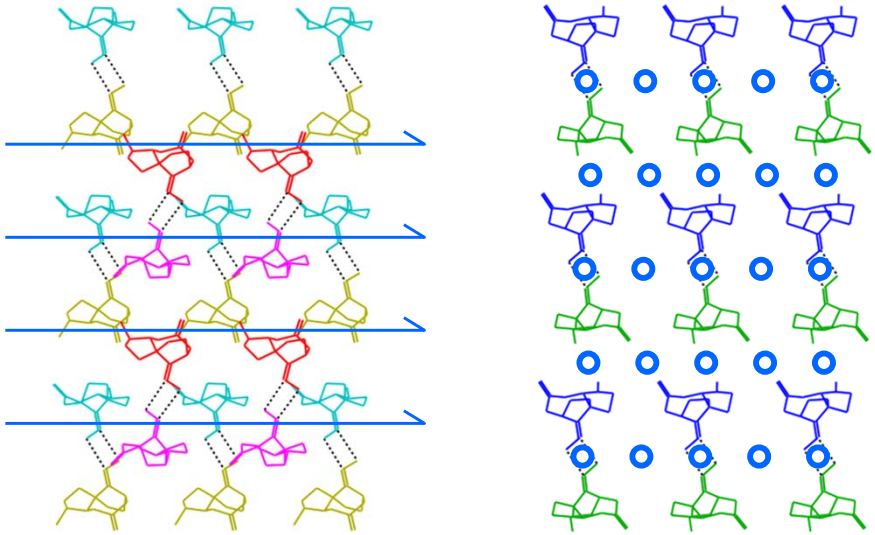
View along **b**



(*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)
(The disorder is not shown)

Layers (001)

$p2_111$, *z*=4, *z'*=2



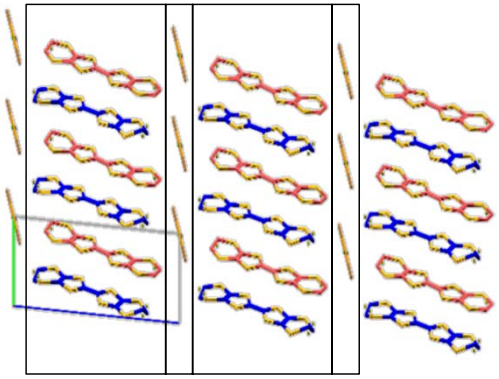
$p\bar{1}$ mimic.
z=2, *z'*=1

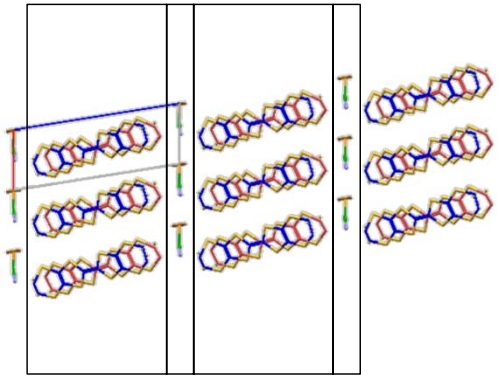
alt layers, 2-D

Views along **a** and **b**

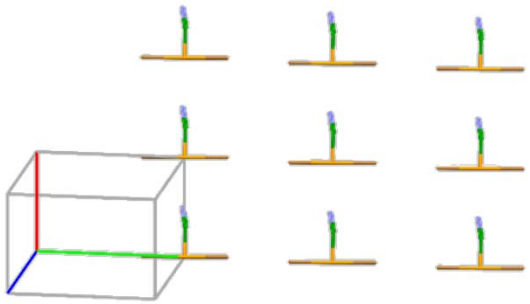
YEMCUO01
(*P*1, *Z*=1)

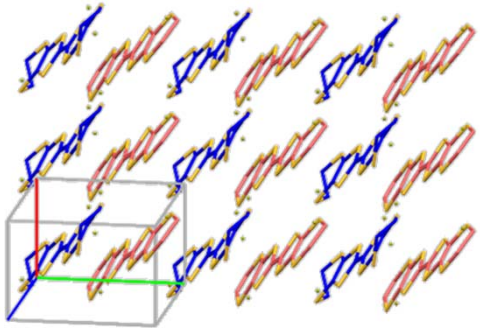
1:1:1 BEDT-TTF cation, its neutral molecule, and a Br_2SeCN anion





Layers (001)





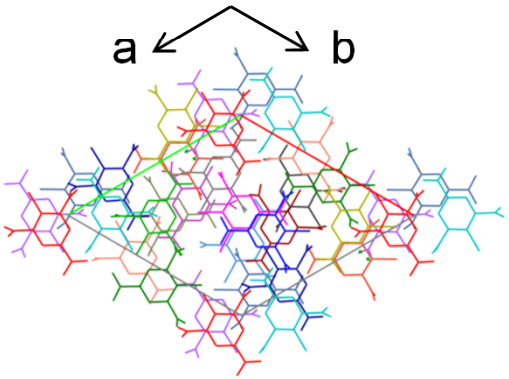
*p*211, *z*=2, *z'*=1
(or even *pm*2*m*, *z*=1, *z'*=¼)
axes [100], [010], angle 92.1°

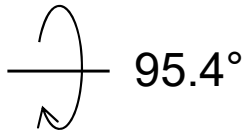
p$\bar{1}$, *z*=2, *z'*=1
(cation, molecule considered to be equivalent)

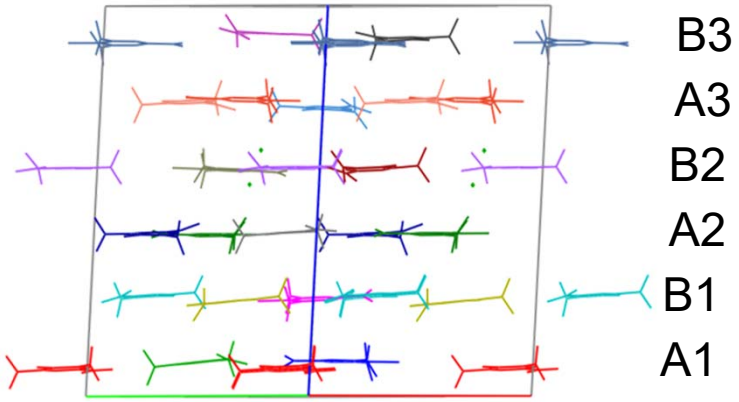
alt layers, 2-D

ZZZVXQ06
(*P*1, *Z*=18)

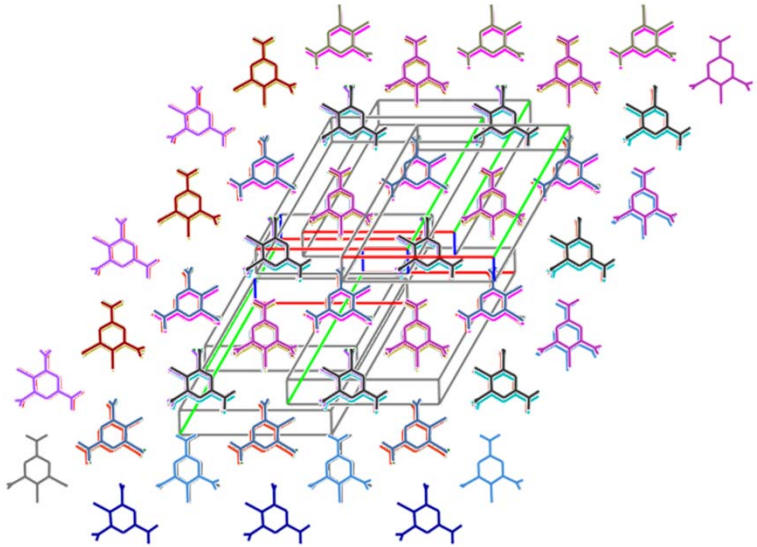
View along **c**





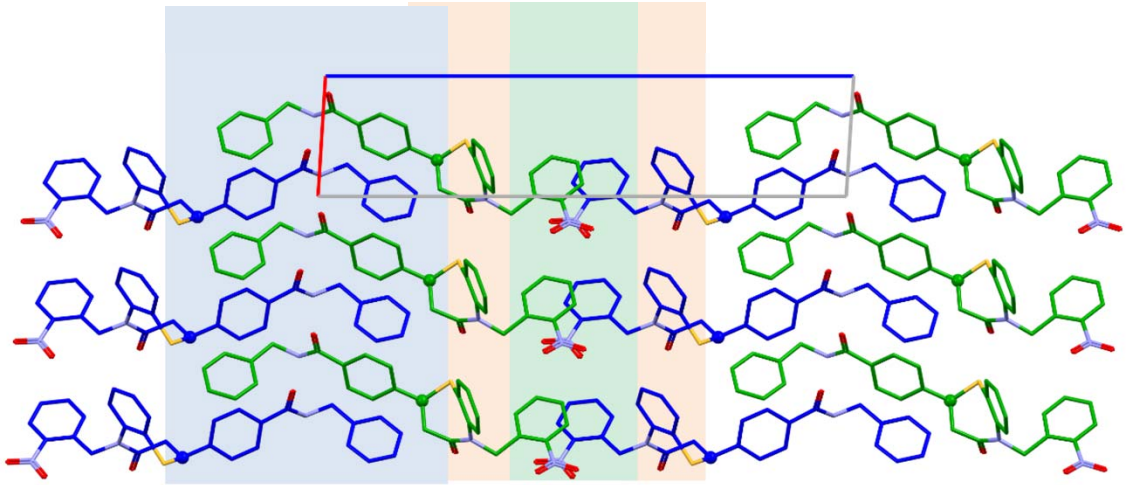


Overlay by translation of the six independent layers (001) after rotation of layers B1, B2, and B3 by 180° around the layer normal



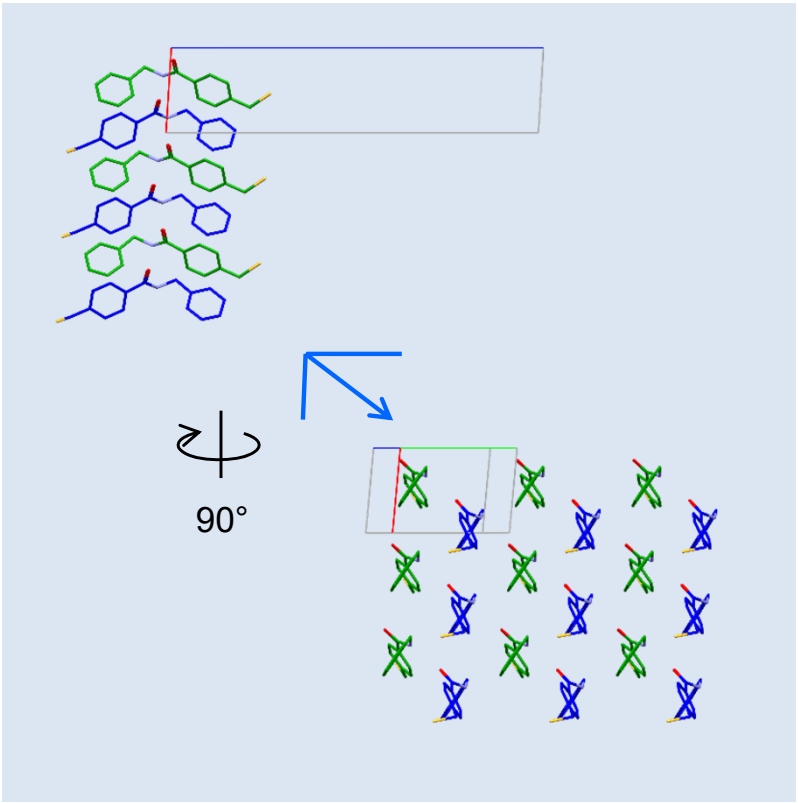
Structures that have hybrid packing

hybrid packing

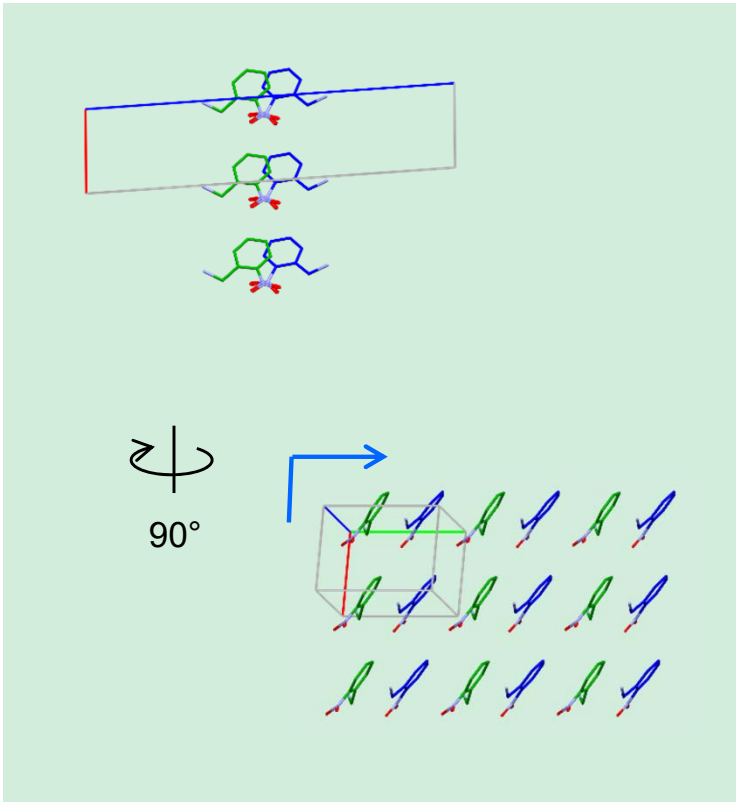


BINHEO
(*P*1, *Z*=2)

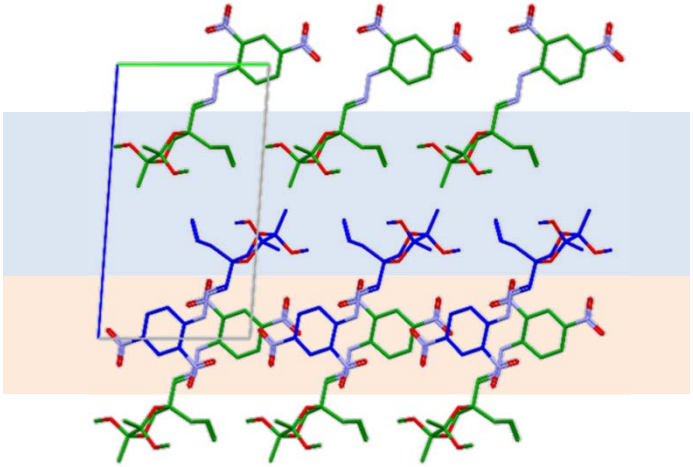
(*p*11[110] is *p*11*n*)



(standard setting of *p*11*b* is *p*11*a*)



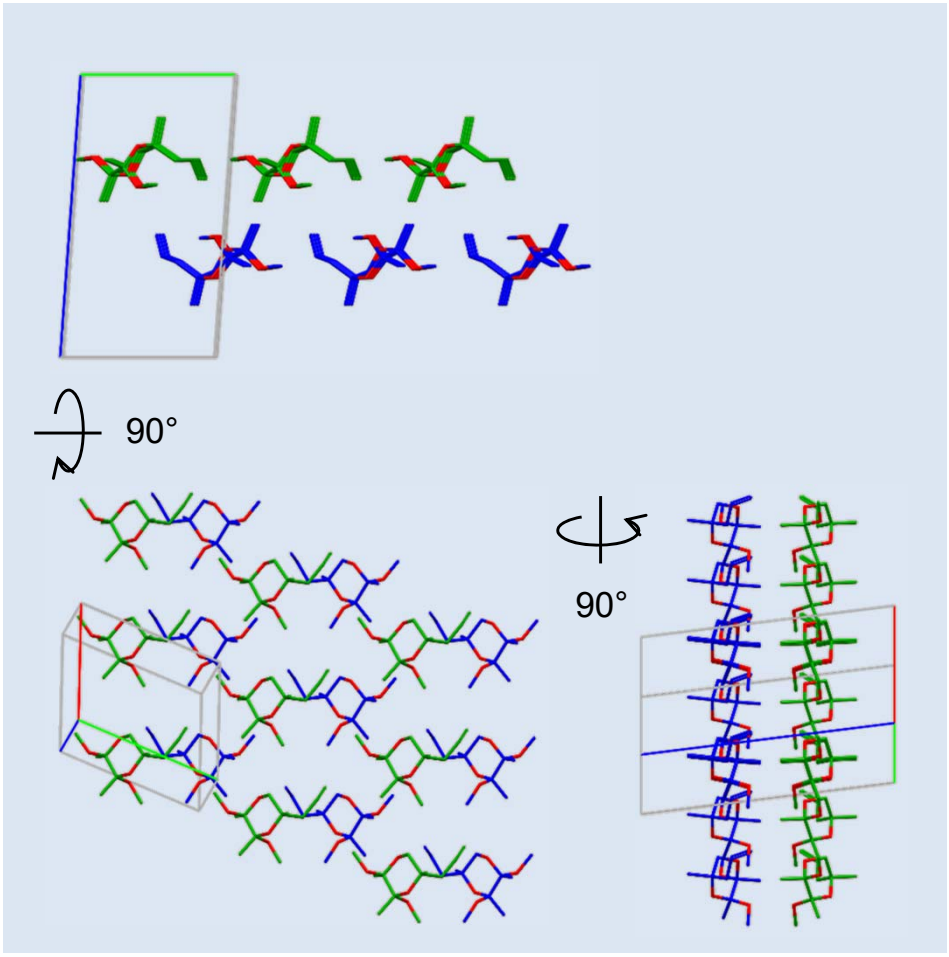
hybrid packing

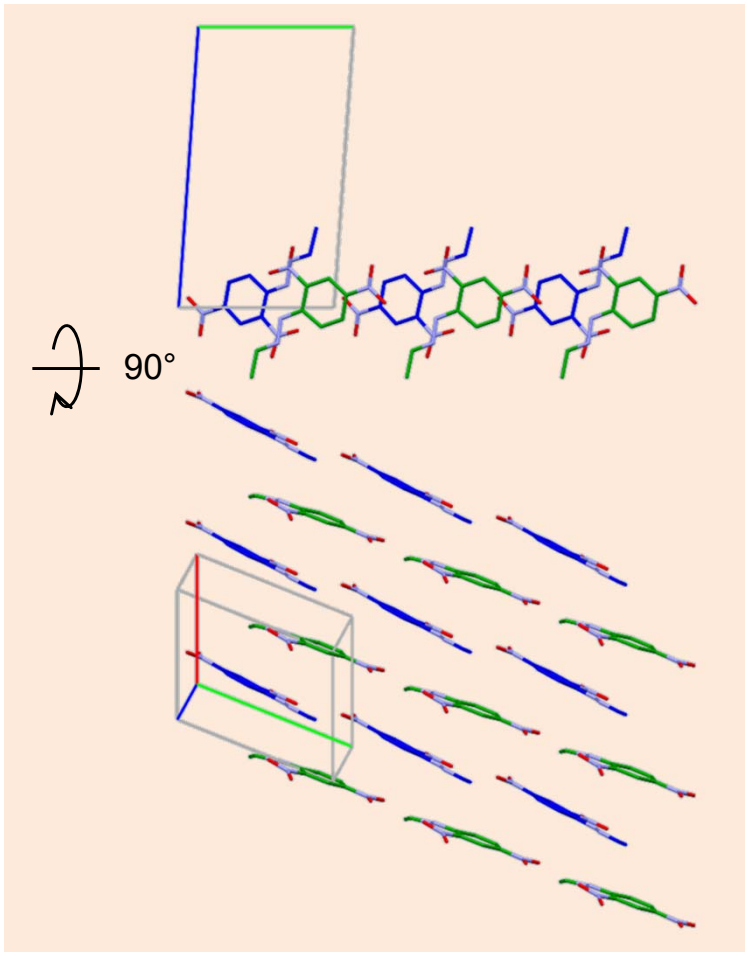


EGOTOK
(*P*1, *Z*=2)

*c*211

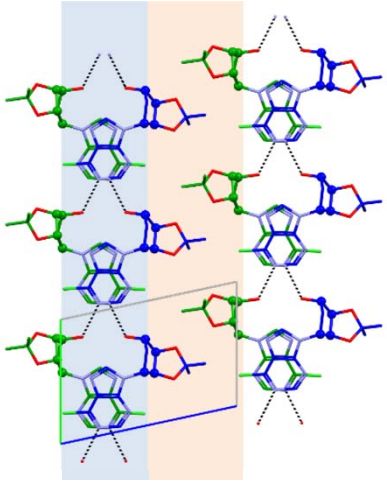
$p\bar{1}$



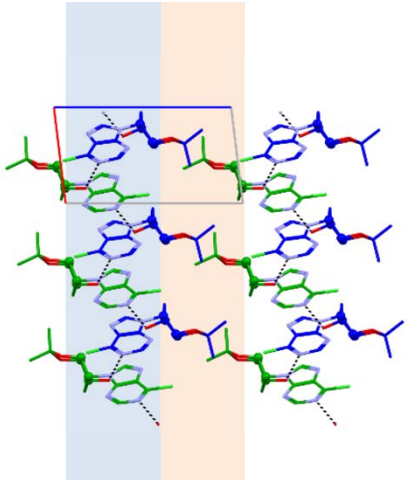


hybrid packing

views along
a and **b**

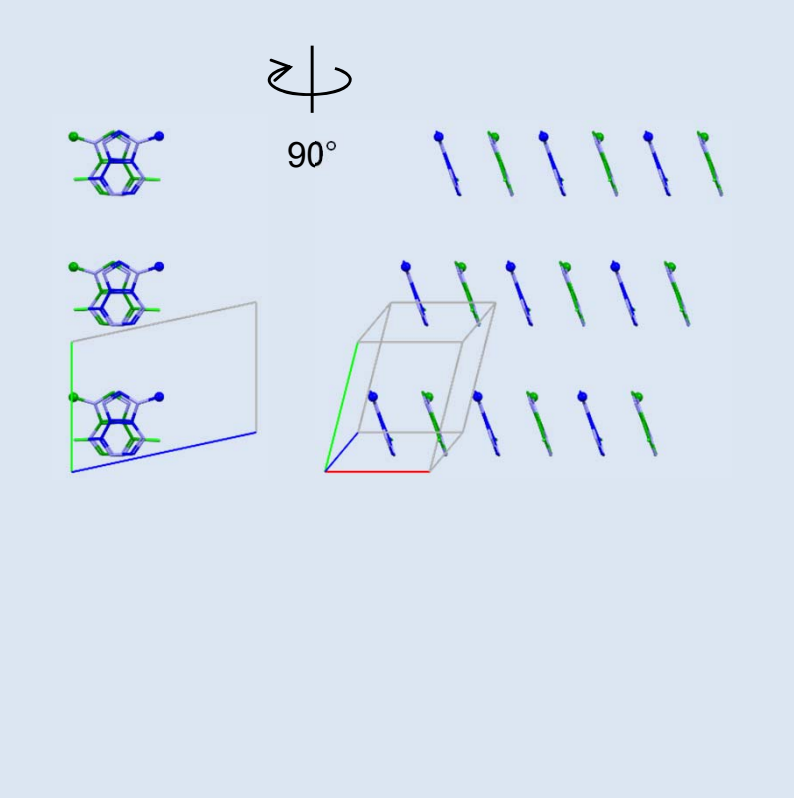


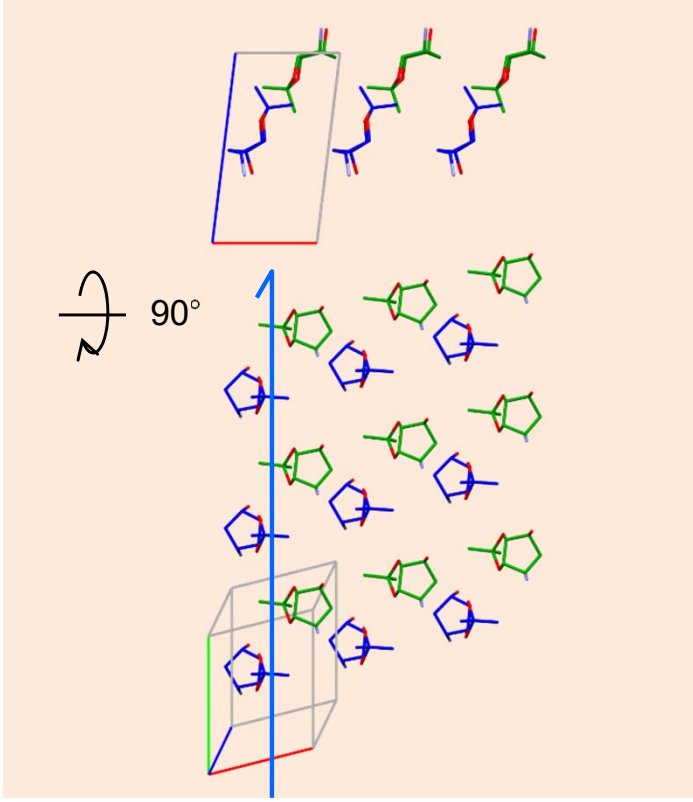
*p*11*a* $p2_1$
(1-D only)



*p*11*a* $p2_1$
(1-D only)

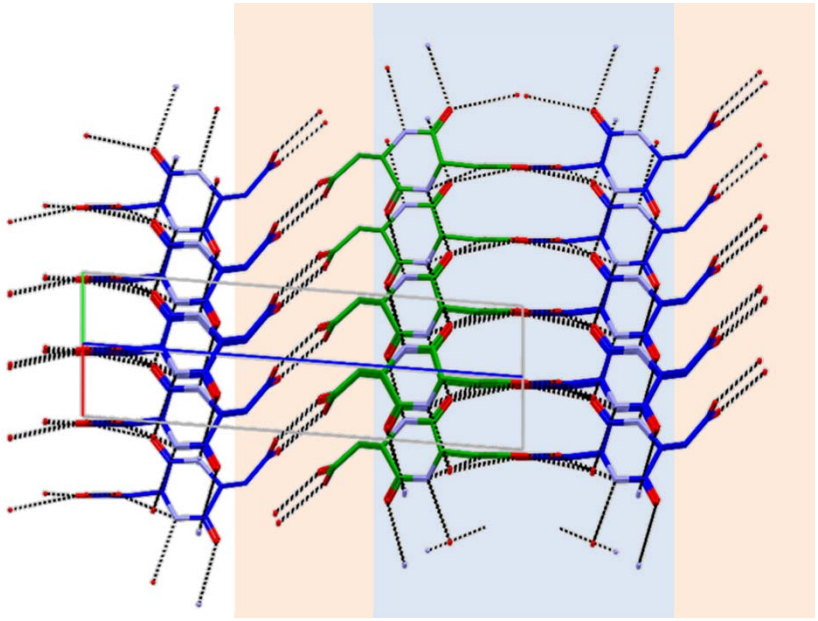
JEMHEP
(*P*1, *Z*=2)



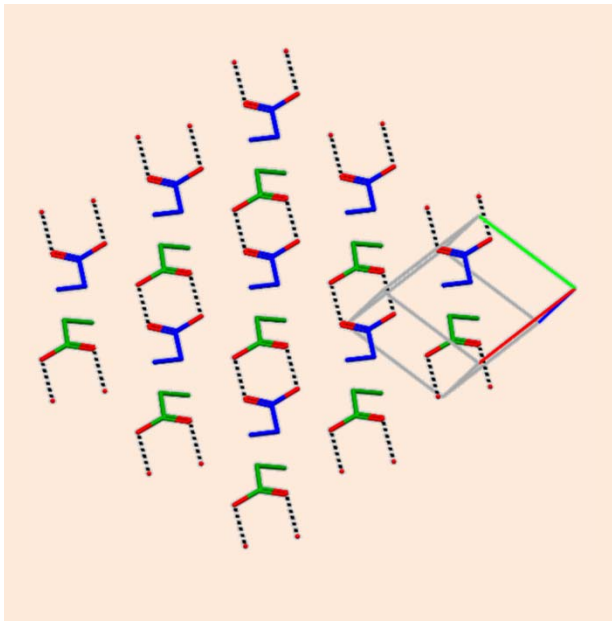


hybrid packing

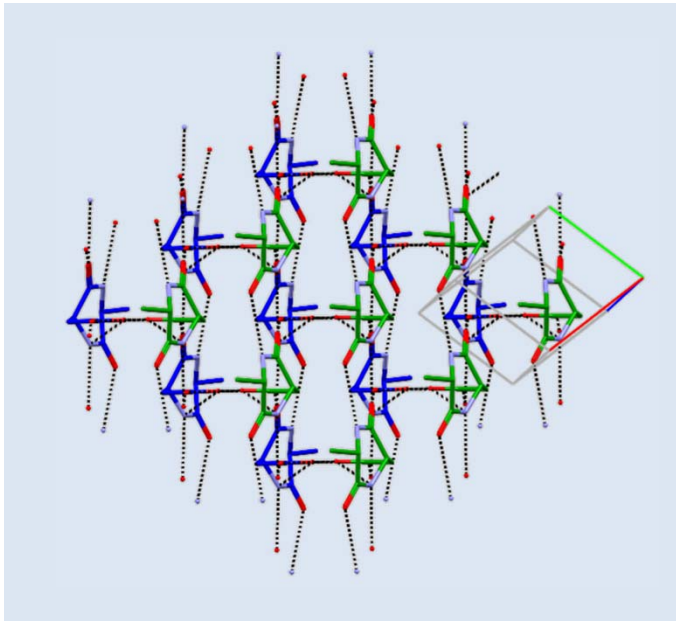
PAXNIL02
(*P*1, *Z*=2)



$p\bar{1}$ $c211$



90°



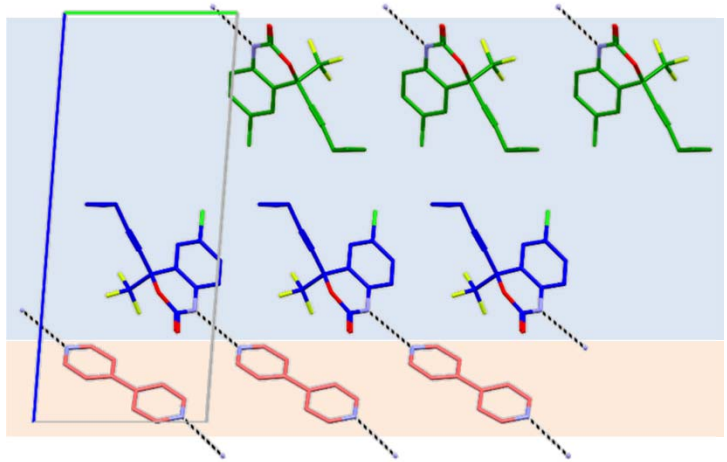
hybrid packing

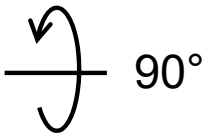
QUSQOL
(*P*1, *Z*=2)

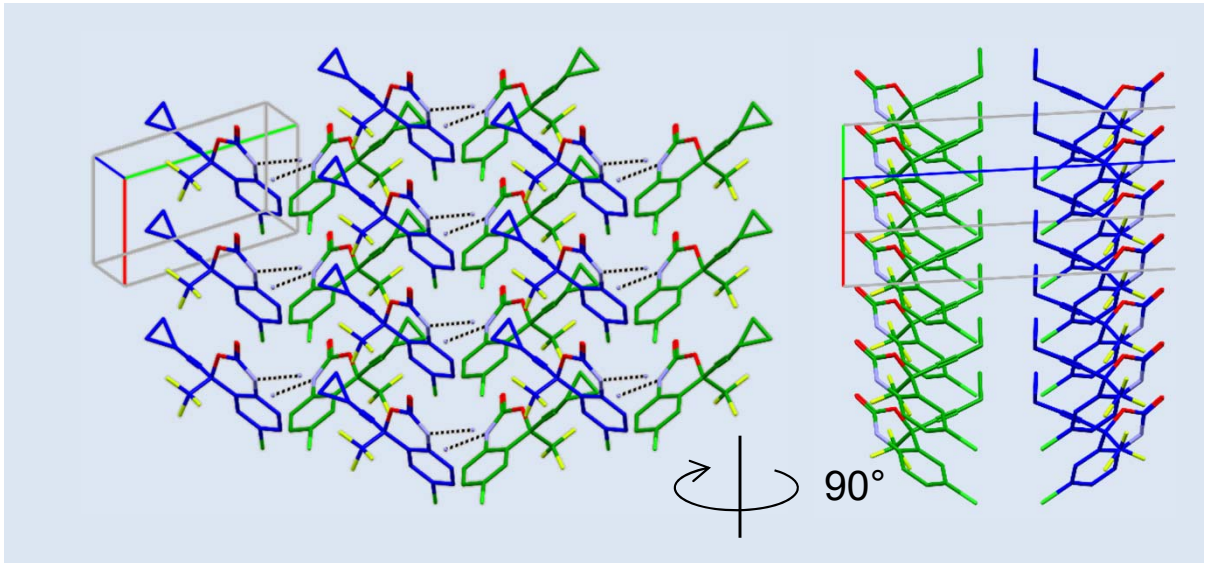
(Formulated as a 1:½ co-crystal; *Z* would be 1 for a 2:1 formulation)

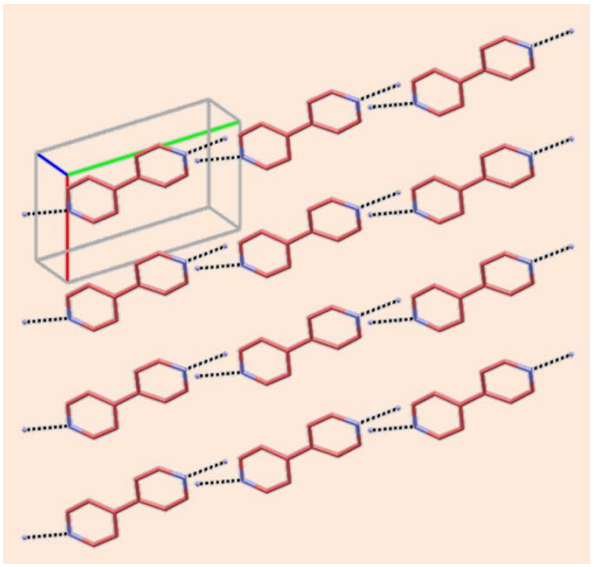
*c*211

$p\bar{1}$



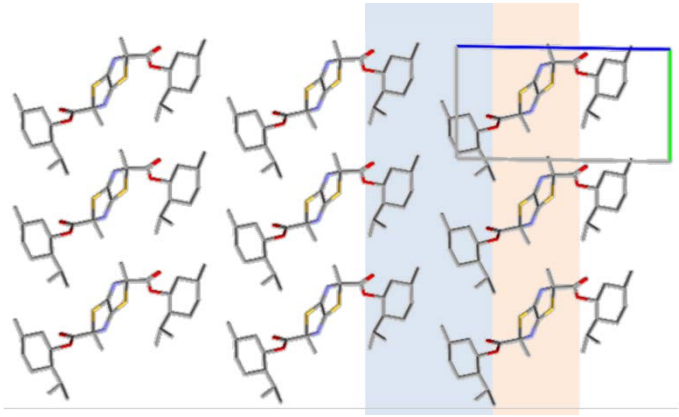






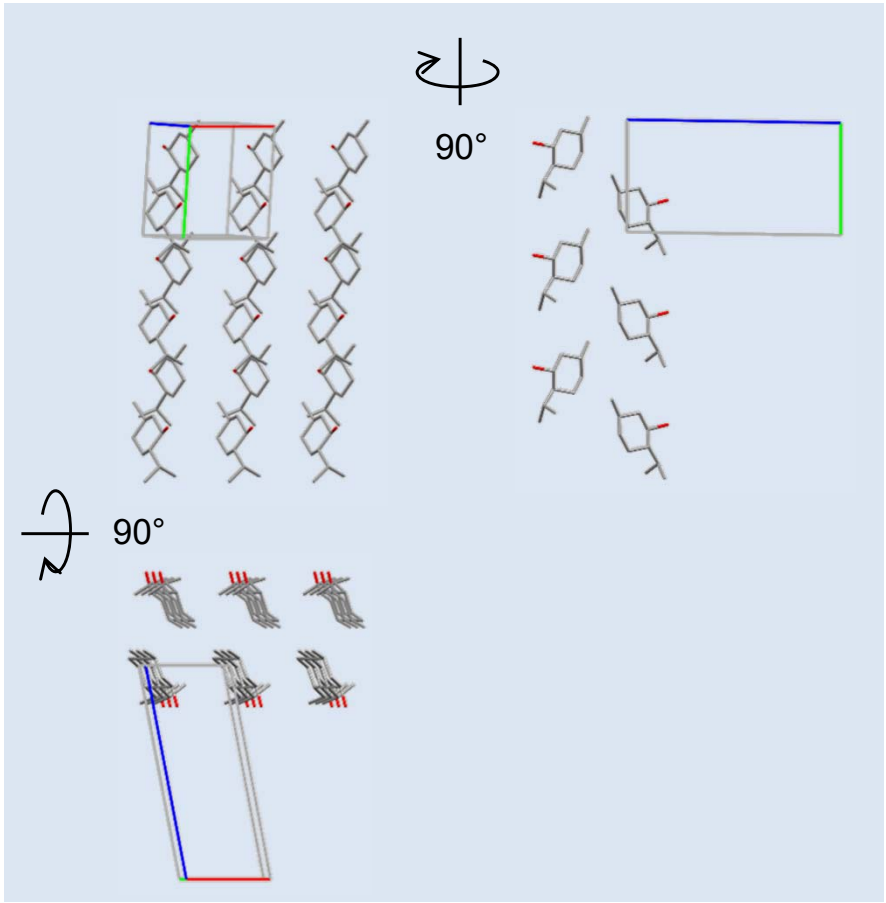
The bipyridine molecules lie on approximate inversion centers

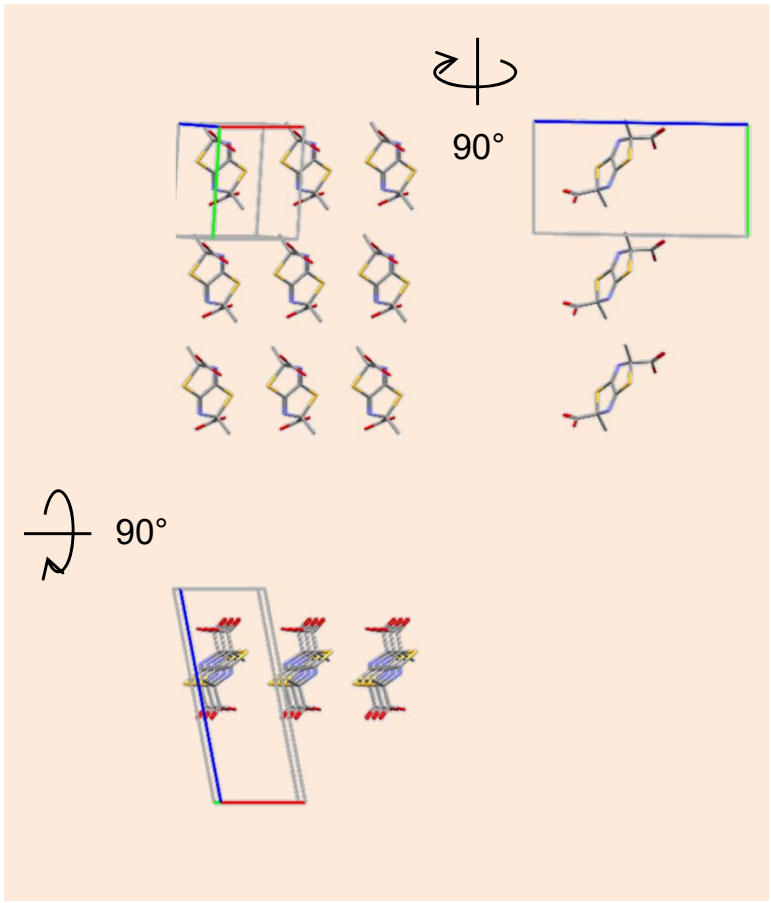
hybrid packing



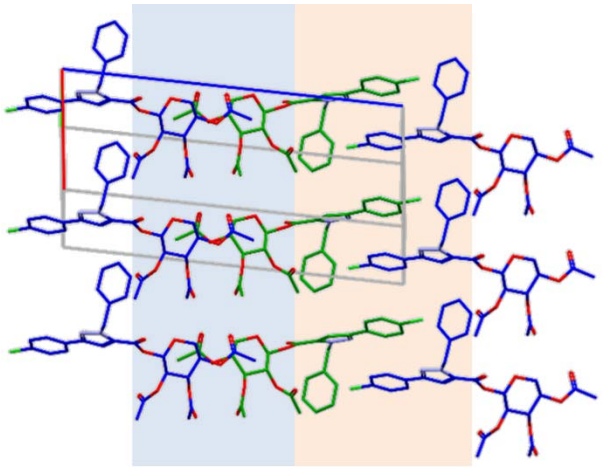
REBNAP
(*P*1, *Z*=1)

$p2_111$ $p\bar{1}$



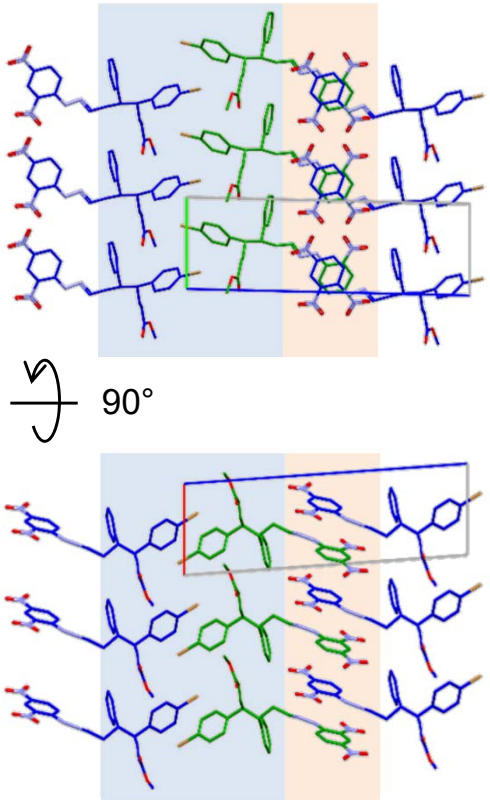


Additional examples of hybrid packing



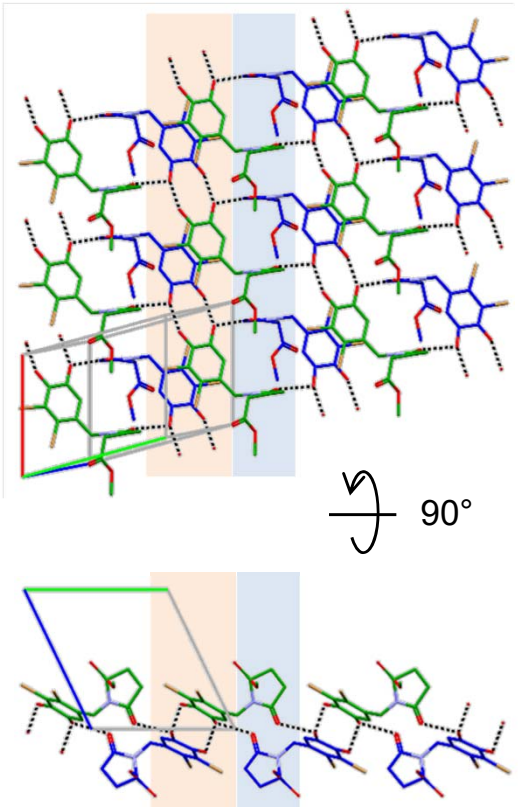
CAKQUC

2 along **a** near *z*=0.4;
$\bar{1}$ near *z*=0.9



IXOJAG

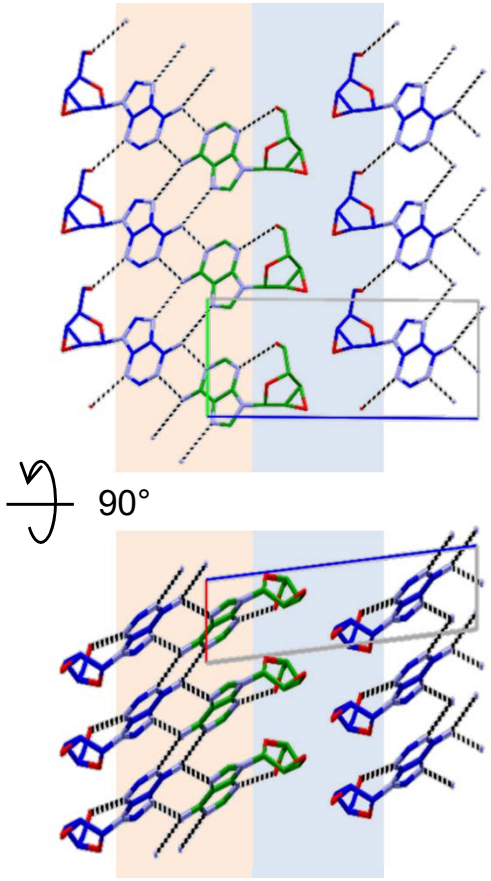
2_1 along **b** near *z*=0;
$\bar{1}$ near *z* =½



MASDOA

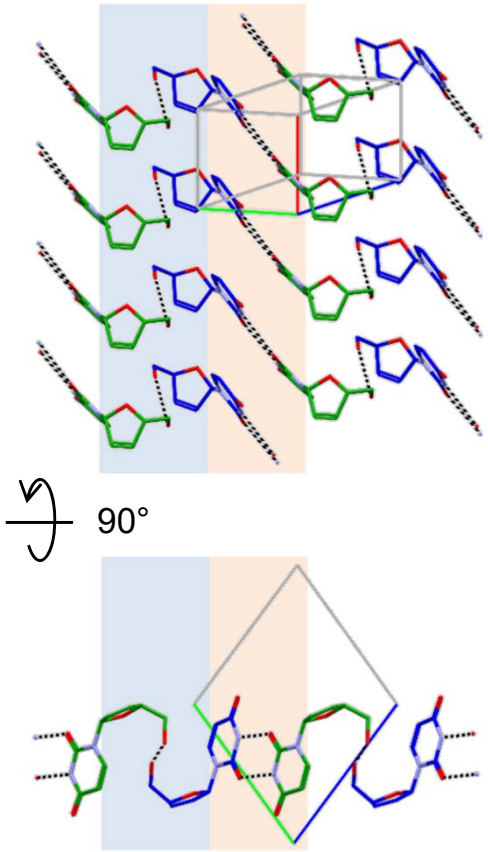
$\bar{1}$ near *y*=¾;
2_1 along **a** near *y*=1¼

Yet more examples of hybrid packing



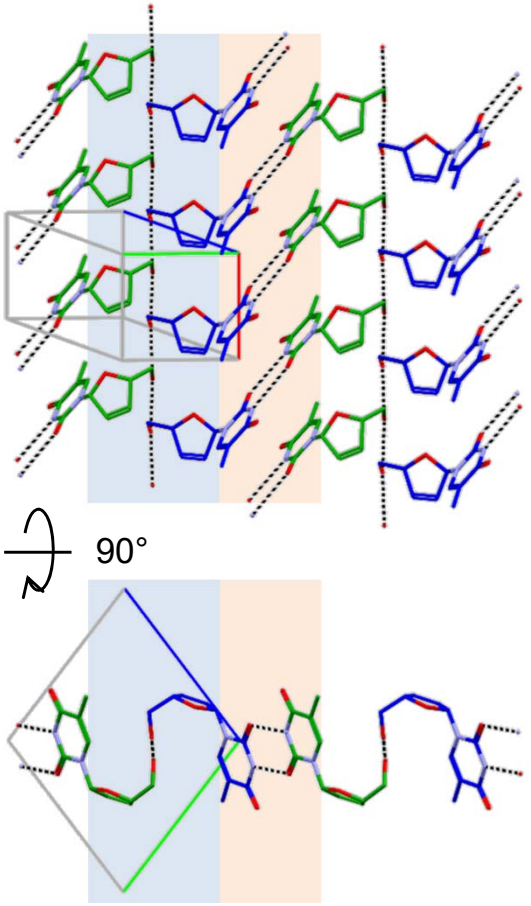
VOMFOS

$\bar{1}$ near *z*= -0.1;
2_1 along **b** near *z*=0.4



WAXLEM

layer (011)
2_1 along **a**; (ribose groups);
$\bar{1}$ (uracil groups)



YACTEC01

layer (01$\bar{1}$)
2_1 along **a**; (ribose groups);
$\bar{1}$ (thymine groups)

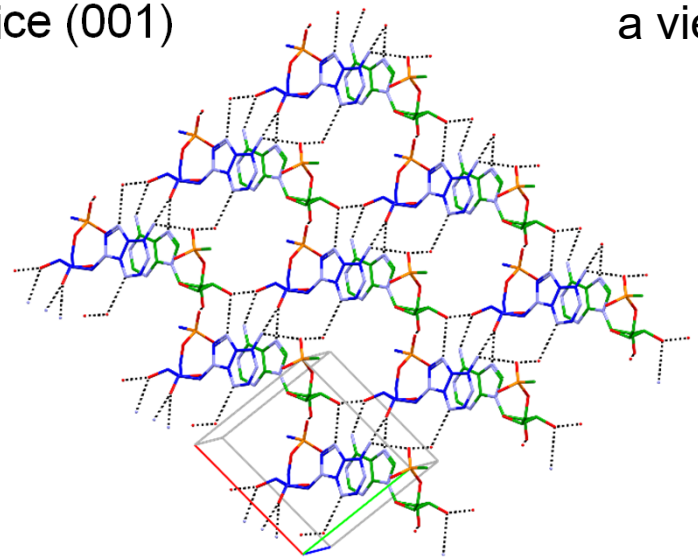
Structures that have borderline approximate symmetry

very distorted, but still easily recognizable, *C*2

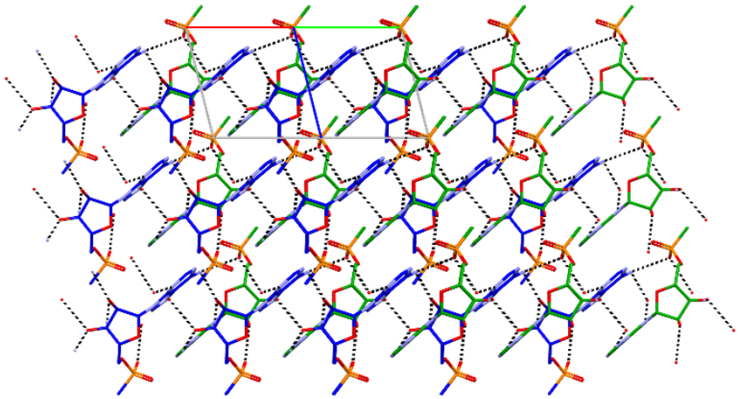
ADMPOT10
(*P*1, *Z*=2)
(a hemihydrate)

*C*2, *Z*=4, *Z'*=1
axes [110], [1$\bar{1}$0], [001];
angles 86.4, 103.6, and 83.7°
γ is quite far from 90° but the approximate 3-D symmetry easy to see, especially in a slice (001)

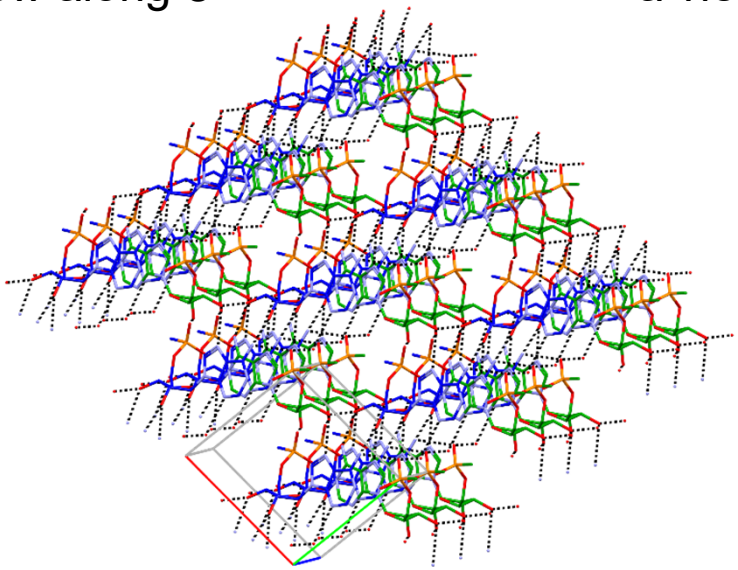
a slice (001)



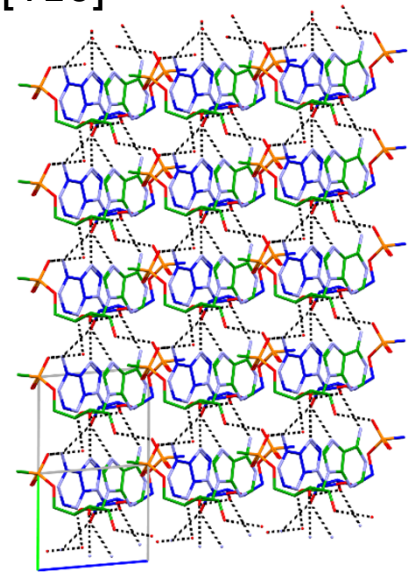
a view along [110]



a view along **c***



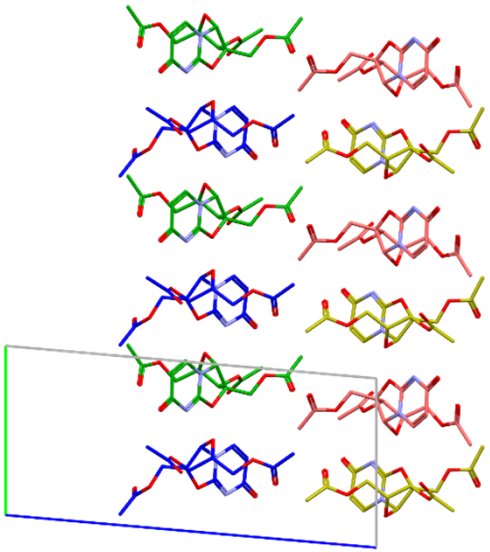
a view along [1$\bar{1}$0]



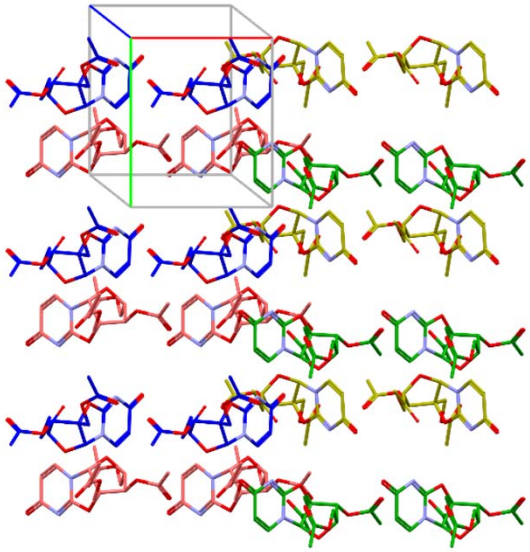
distorted $P2_12_12_1$?

AFONOY
($P1$, Z=4)

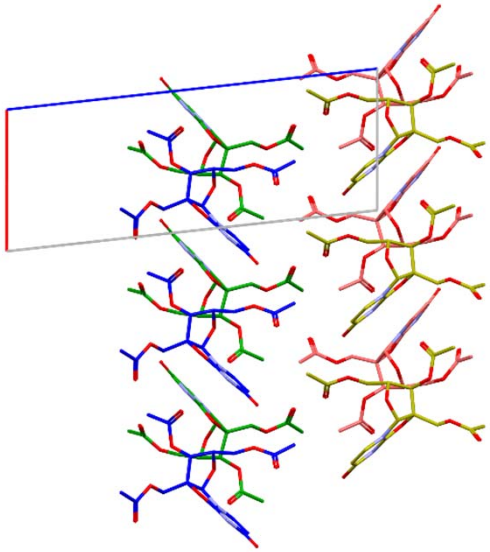
View along **a** showing the approximate 2_1 along **b** that relates #1&2 as well as #3&4



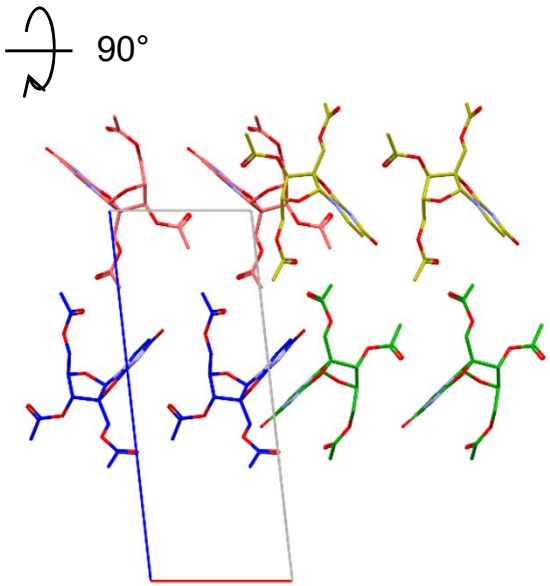
View along **c*** of a layer (001) showing the approximate 2_1 along **c*** that relates #1&4 as well as #2&3 (some molecules removed for clarity)



View along **b** showing the approximate 2_1 along **a** that relates #1&3 as well as #2&4



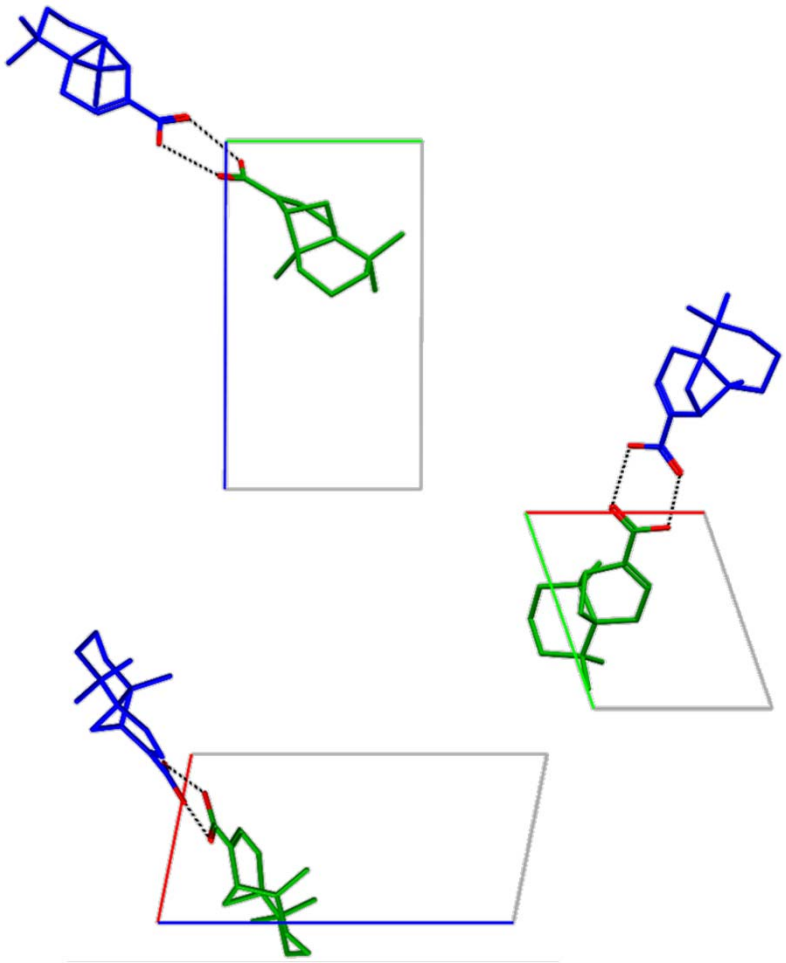
While the cell angles are 95.0, 96.3, 90.0° the approximate $P2_12_12_1$ symmetry is convincing



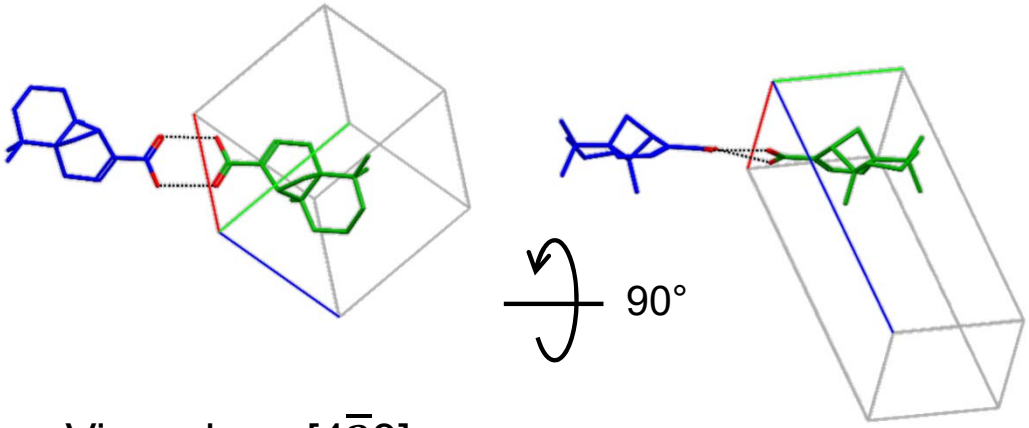
$P\bar{1}$ mimic?

AJOVIG
($P1$, Z=2)

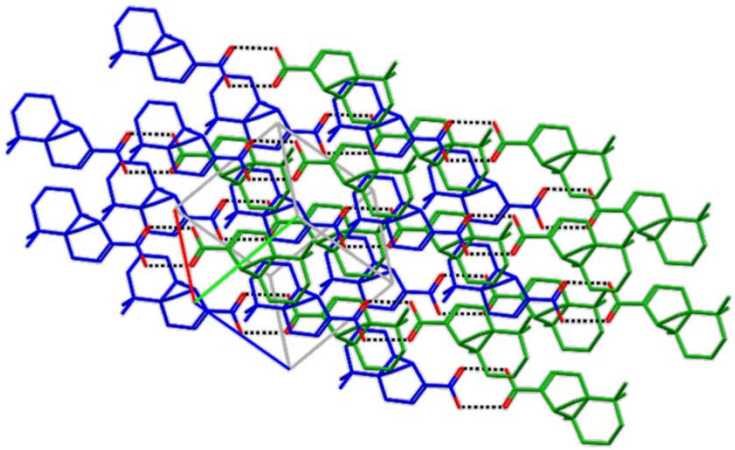
Views along **a**, **b**, and **c**



View along [4$\bar{2}$3]
of two molecules



View along [4$\bar{2}$3]
of more
molecules

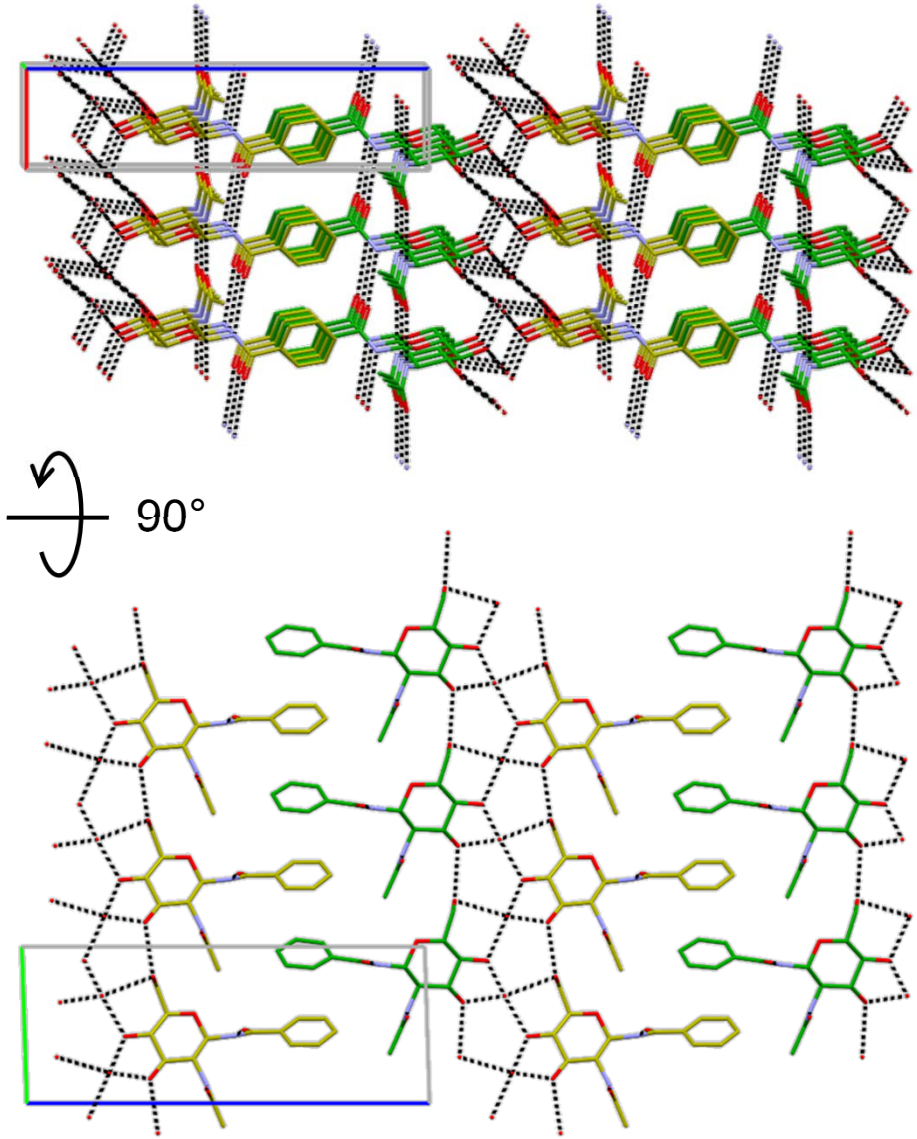


The approximate 2 is local only so classify as a $P\bar{1}$ mimic

distorted $P2_1$ or hybrid packing?

CAKHIF
($P1$, Z=2)

View along **b**,
0<y<3

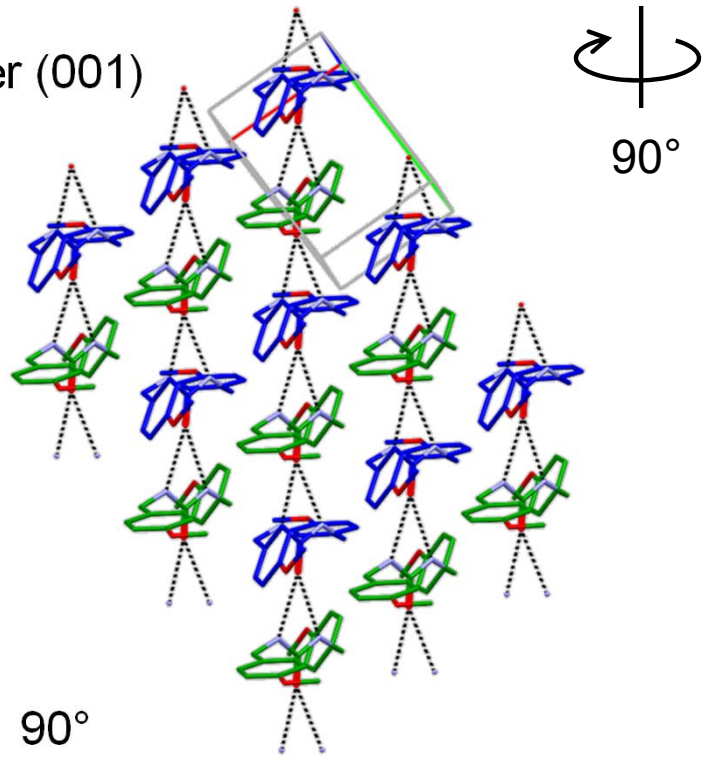


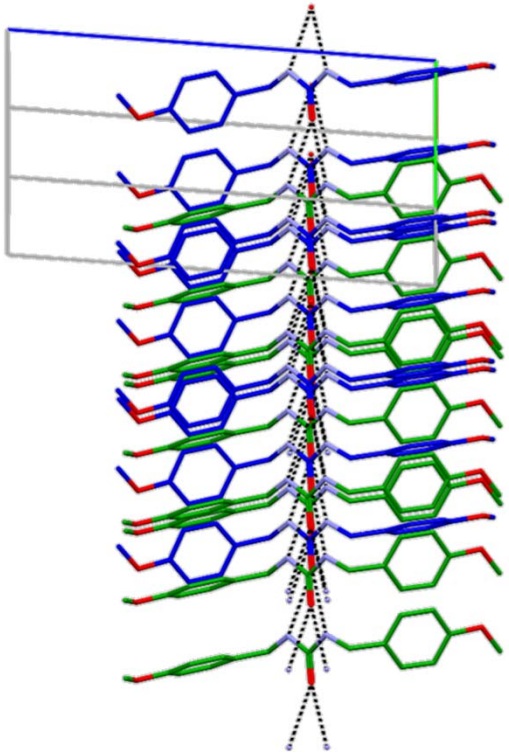
$P2_1$, Z=2, Z'=1
axes [100], [010], [001];
angles 91.8, 90.0 and 92.1°
but
the Ph rings are parallel and therefore related by approximate inversion rather than by the approximate 2_1 axis. Still, the $P2_1$ description seems better.

translation or 1-D 2_1?

EBEPEJ
(*P*1, *Z*=2)

Layer (001)





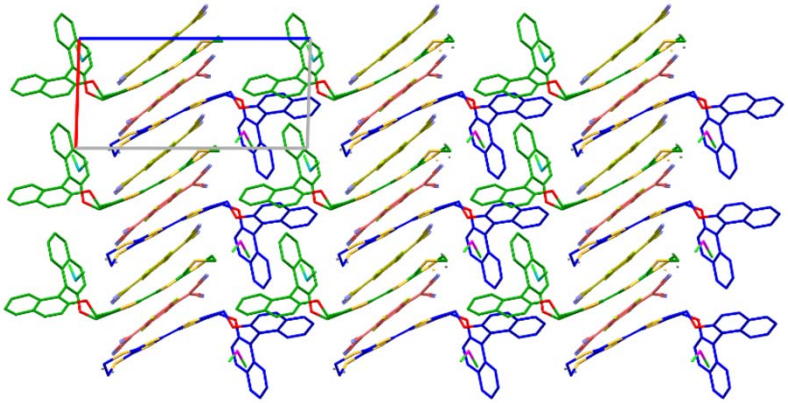
The molecule could have twofold symmetry but the Ph ring rotations differ. The approximate 2_1 along [110] is very good but the offset of H-bonded columns means approximate 2_1 symmetry can be 1-D only. Approximate translation seems a better description

very distorted, but still easily recognizable, *C*2

EPIYUY
(*P*1, *Z*=2)

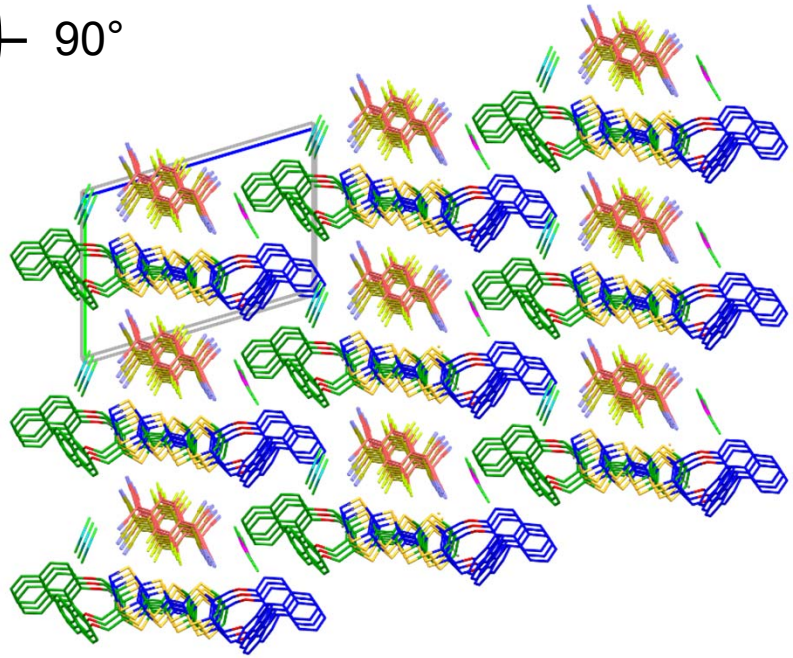
(a 1:1:1 solvated co-crystal)

View along [010]



*C*2, *Z*=4, *Z'*=1
axes [012], [0$\bar{1}$0], [100];
angles 87.3, 91.9, and 96.6°
γ is quite far from 90° but the approximate 3-D symmetry is obvious

90°



[0$\bar{1}$0]

96.6°

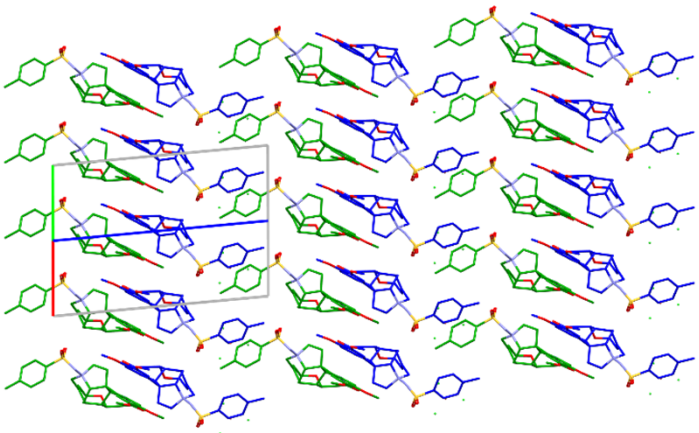
[012]

very distorted, but still easily recognizable, *F*2

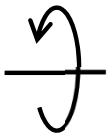
GEGYAV
(*P*1, *Z*=2)

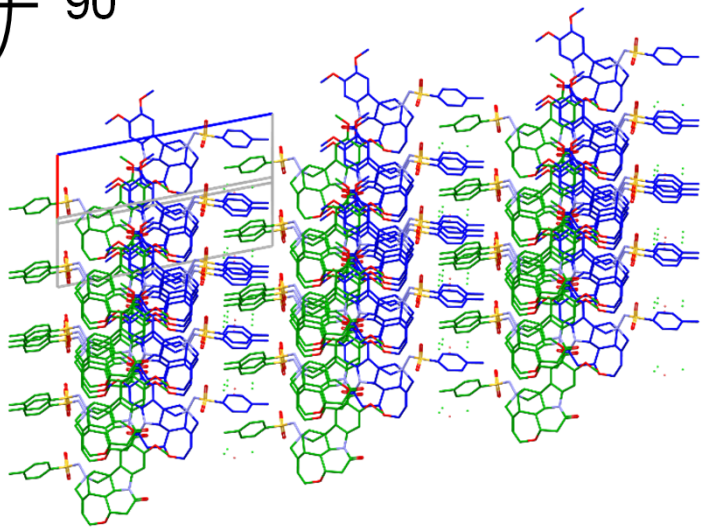
(a 1:2 solvate;
$CHCl_3$s not shown)

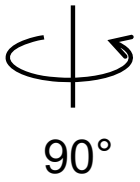
View along [110]

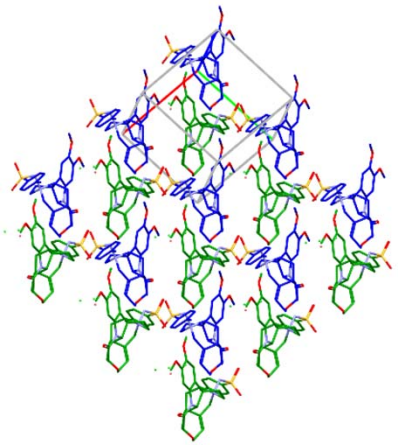


*F*2, *Z*=8, *Z'*=1
axes [112], [$\bar{1}\bar{1}0$], [$1\bar{1}0$];
angles 87.9, 95.4, and 96.6 °
γ is quite far from 90° but the approximate
3-D symmetry is obvious









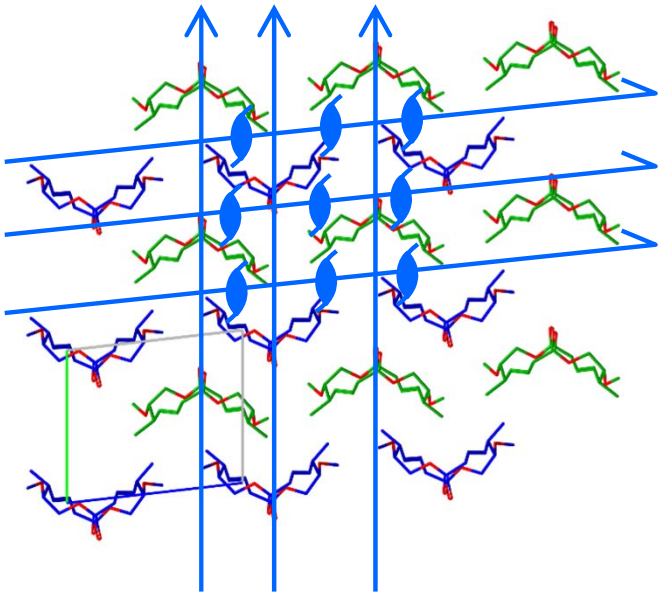
0≤*z*≤1 to show
centering in a
slice (001)

distorted $P2_122_1$, Z'=½?
(standard setting is $P2_12_12$)

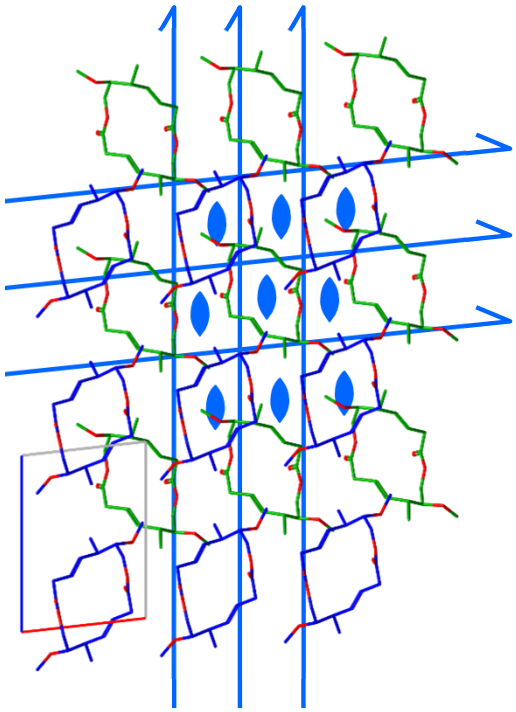
IHOXUY
($P1$, Z=2)

While the cell angles (82.6, 82.7, 82.1°) are all quite far from 90°
the approximate symmetry is too compelling to ignore
and no one layer has better approximate symmetry than does the structures as a whole

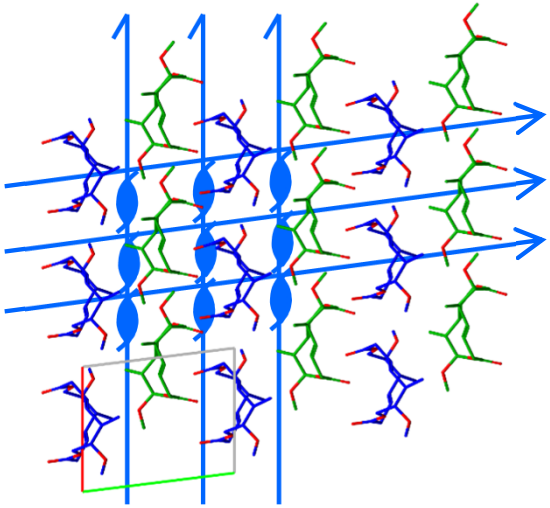
View along **a**



View along **b**



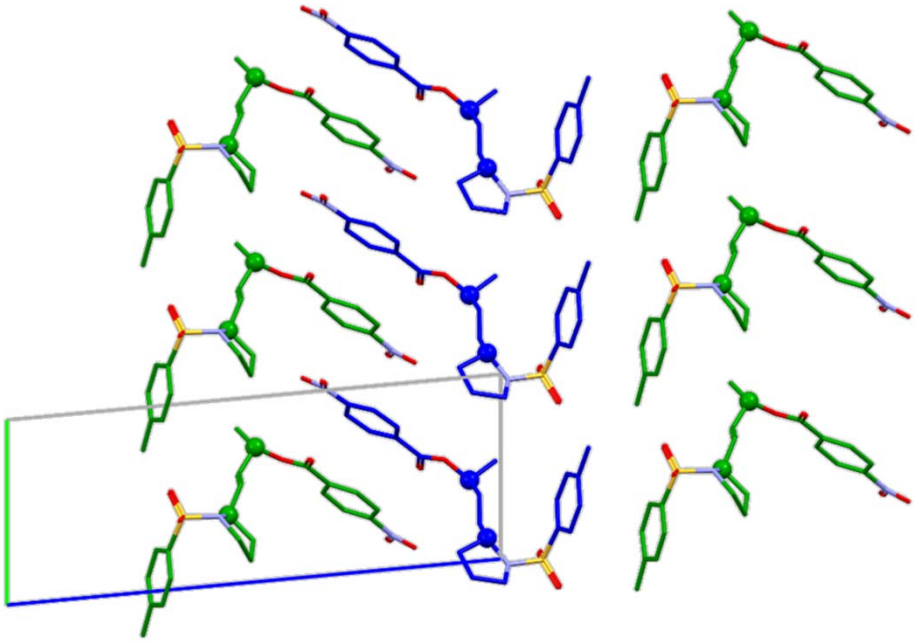
View along **c**

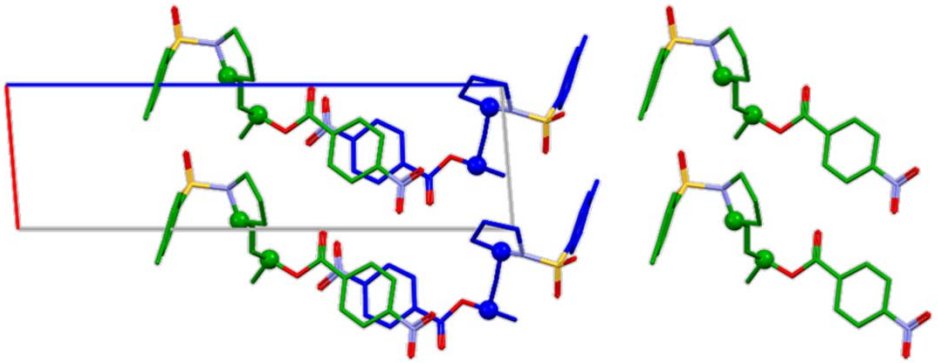


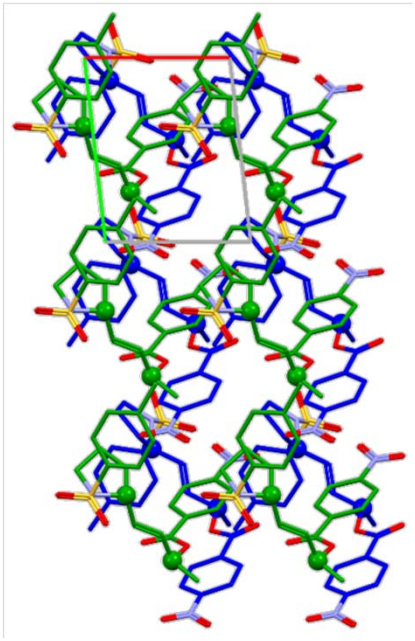
$P\bar{1}$ mimic?

JUSZOO
($P1$, Z=2)

Views along **a**, **b**, and **c**





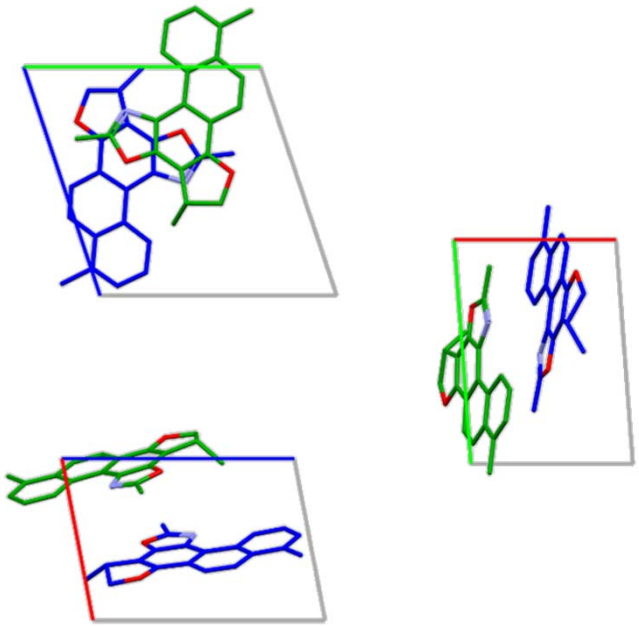


The central CMeCH=CH group and the atoms of the C_4N ring are not related by the approximate inversion or by any other approximate symmetry. The two $\bar{1}$ s are separated by [0.49, 0.42, 0.00] and the conformations differ so the $P\bar{1}$ description seems appropriate

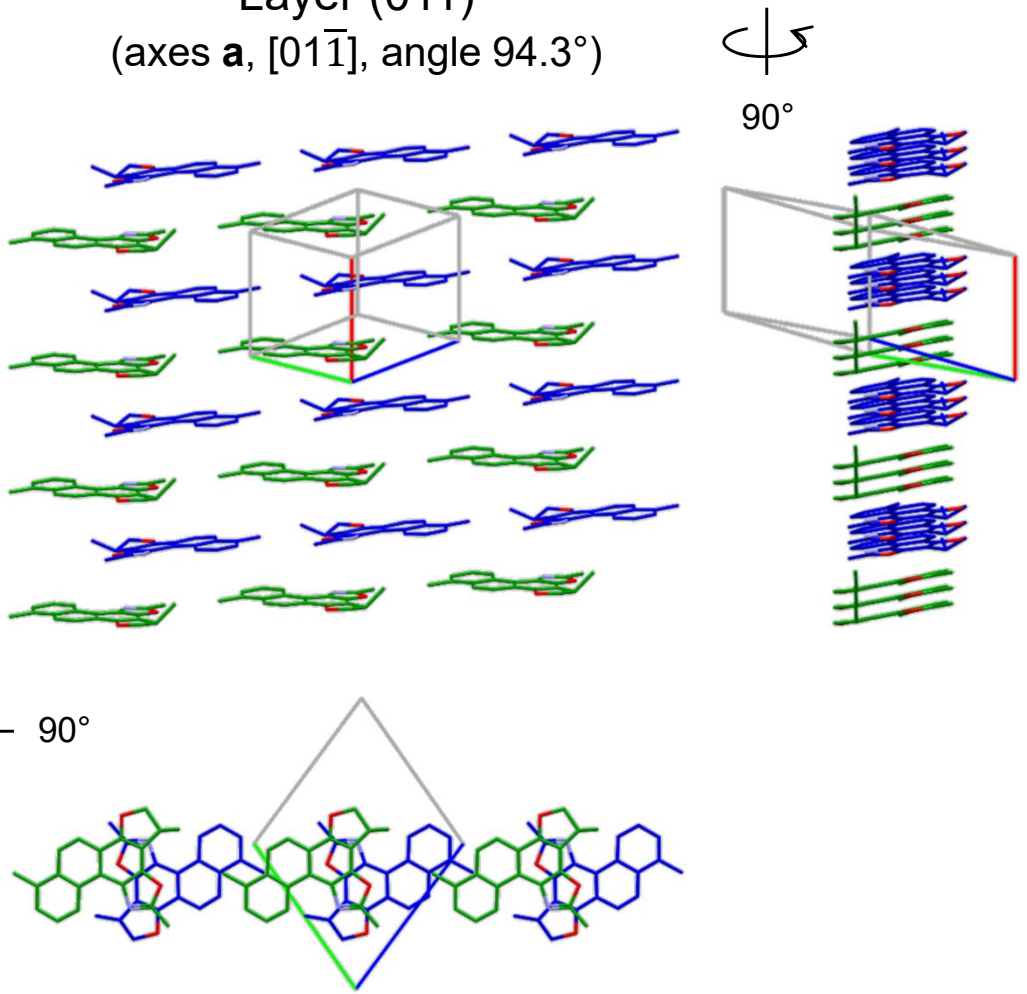
$P\bar{1}$ mimic or $p2_111$ (2-D)?

MEMBAK
($P1$, Z=2)

Views along **a**, **b**, and **c**



Layer (011)
(axes **a**, [01$\bar{1}$], angle 94.3°)



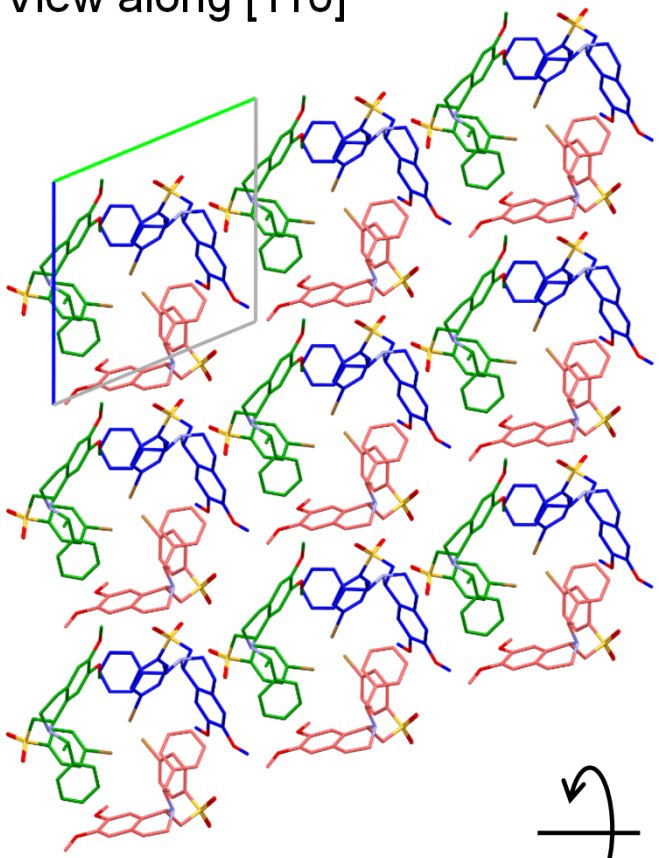
Molecules are planar except for the Me group so both descriptions are possible, but the molecular tilts around [01$\bar{1}$] favor the $P\bar{1}$ description

very distorted, but still easily recognizable, $P3_1$

MOMVOA
($P1$, Z=3)

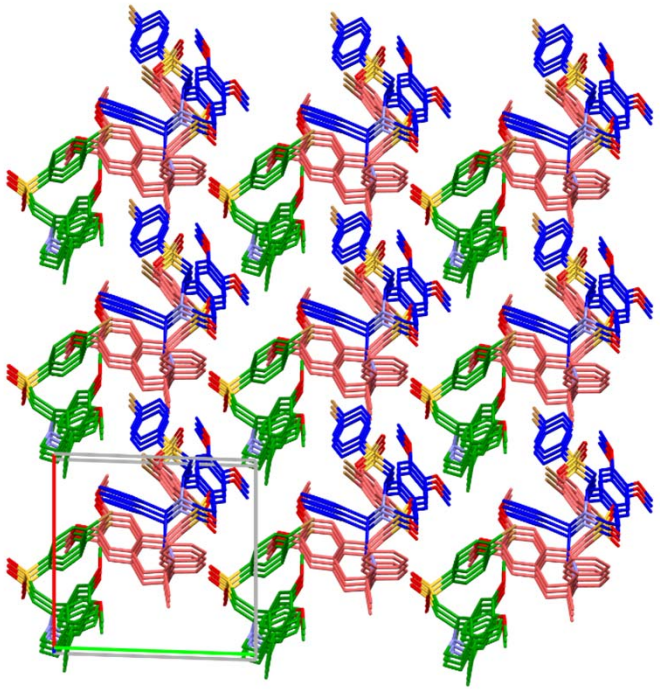
(a 1:⅓:⅓ double solvate;
solvents not shown)

View along [110]



90°

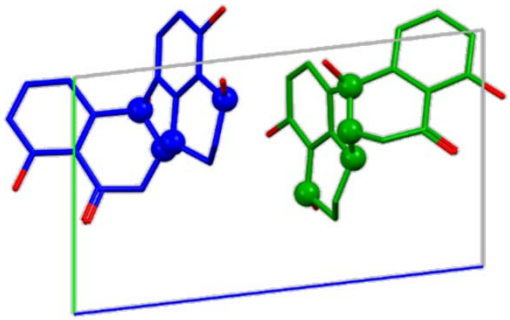
$P3_1$, Z=3, Z'=1
axes [010], [001], [100];
angles 91.5, 91.8, and 112.5 °
γ is quite far from 120° but the approximate
3-D symmetry is easily seen although the 3_1s along
the long cell diagonal are very distorted

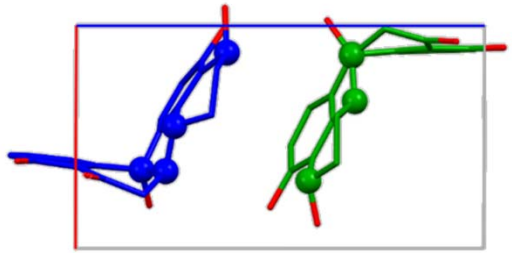


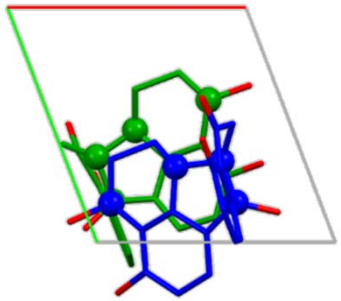
$P\bar{1}$ mimic?

NOLFIF
($P1$, Z=2)

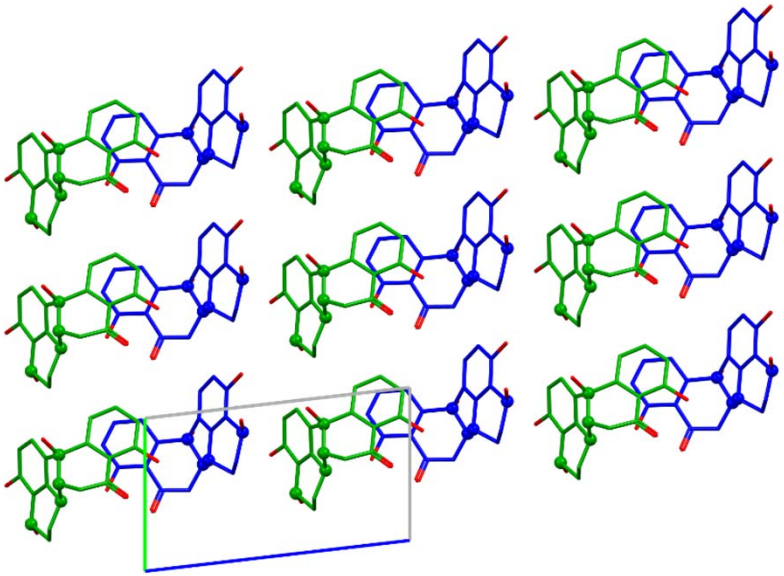
Views along **a**, **b**, and **c**







View along **a** of the structure

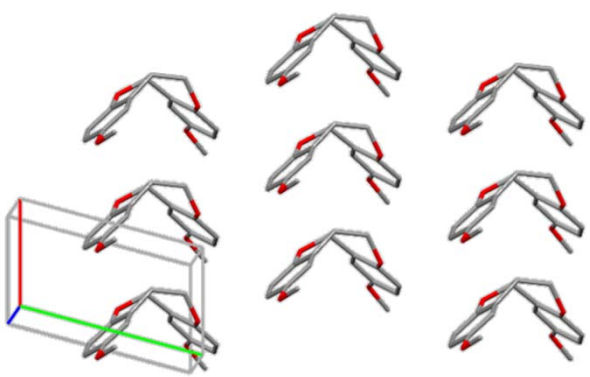


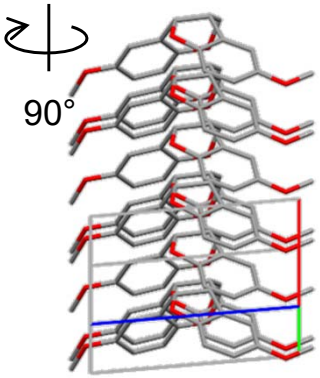
There seems as if there might be an approximate 2 near **b** but it is local only. The $P\bar{1}$ description is better but it is borderline

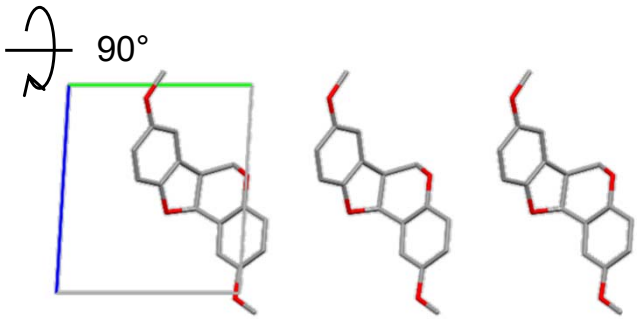
2&2$_1$ mimic, 2-D or 3-D?

PAPLAU
(*P*1, *Z*=1)

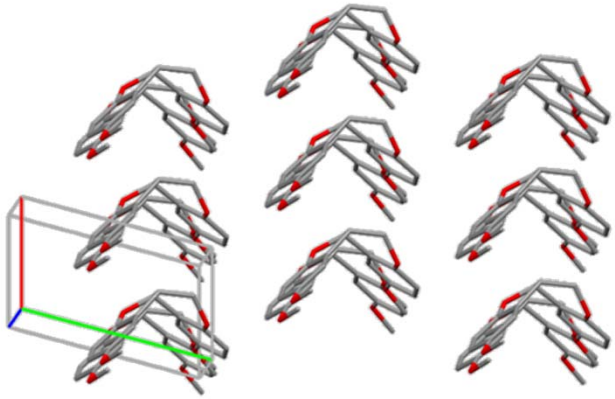
View of a layer (001)







Two layers (001)



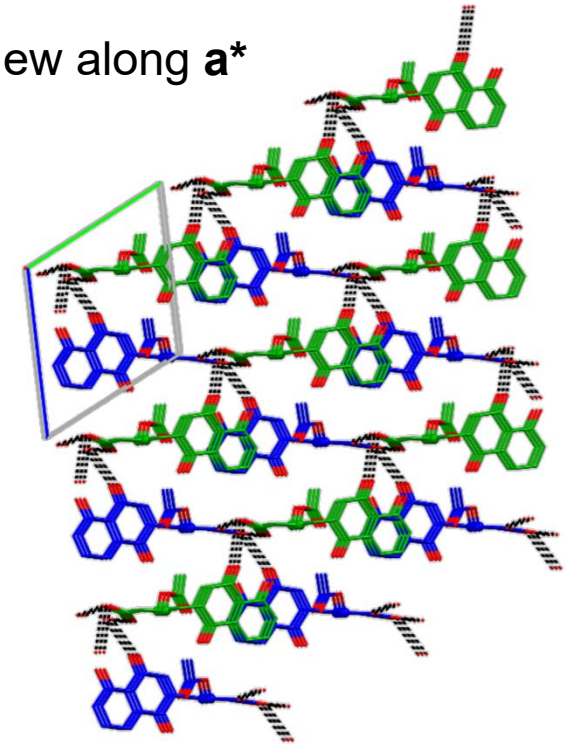
Angles of a *C*2 cell would be 88.0, 103.9, and 94.6° so the approximate symmetry was identified as 3-D

Layer (001)
*c*211, *z*=2, *z'*= ½
axes [100], [120]

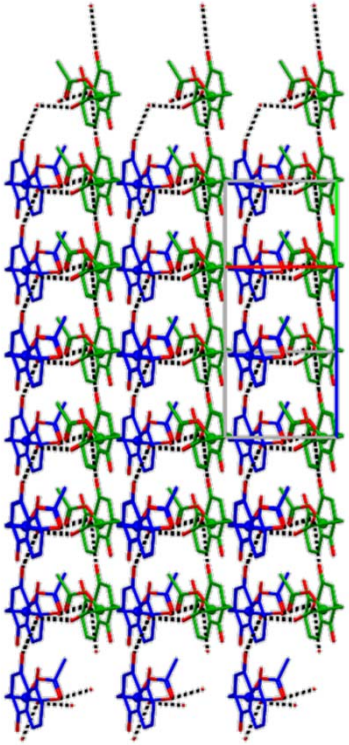
quite distorted, but still obvious, *C*2

ULUHUE
(*P*1, *Z*=2)

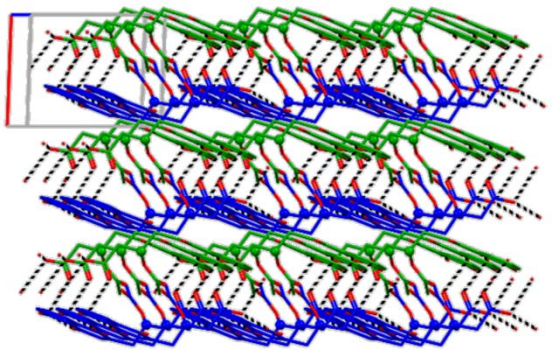
View along **a***



90°



90°



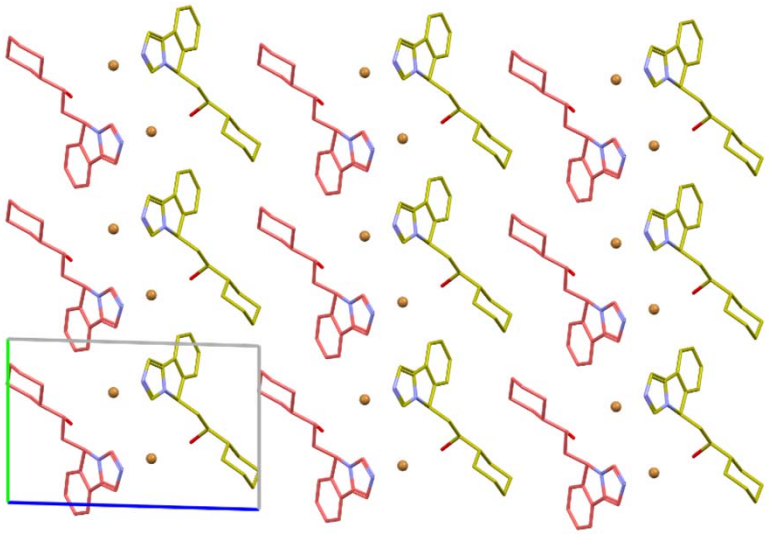
*C*2, *Z*=4, *Z'*=1
axes [021], [001], [100];
angles 90.2, 92.1 and 83.6°
While γ is quite far from 90°
the approximate 3-D symmetry
is very obvious

very distorted, but still easily recognizable, $P2_1$

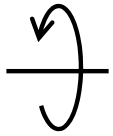
VOJXEA
($P1$, Z=2)

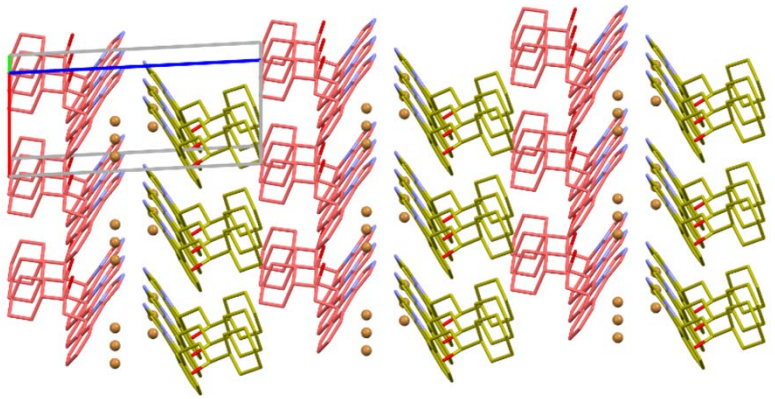
(a Br^- salt)

View along [100]



$P2_1$, Z=2, Z'=1
axes [001], [100], [010];
angles 96.2, 91.3, and 92.9°
α is quite far from 90° but the approximate
3-D symmetry obvious

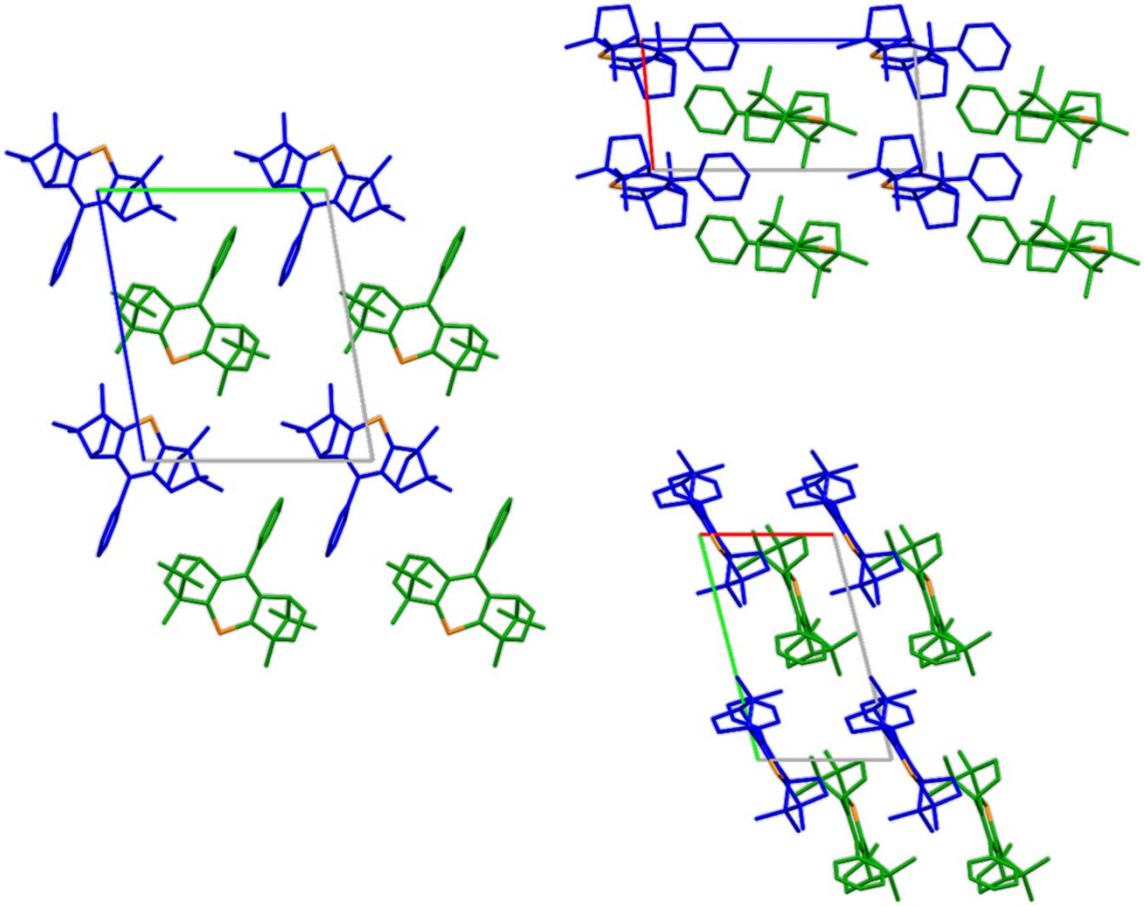




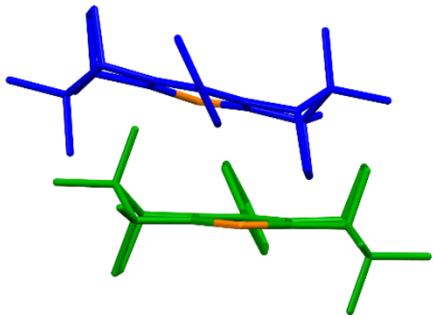
$P\bar{1}$ mimic?

WUKYIL
($P1$, Z=2)

Views along **a**, **b**, and **c**



View along a direction near [01$\bar{2}$]



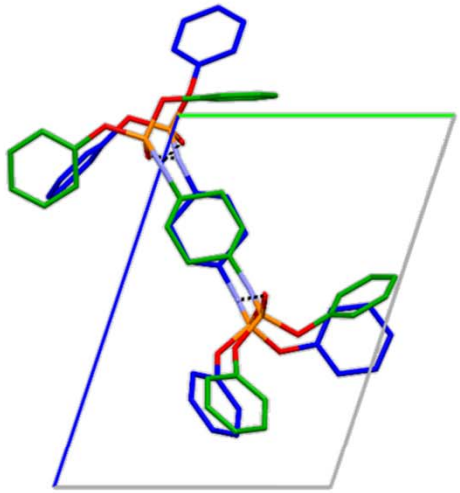
Molecules have approximate twofold symmetry but the direction is not simple

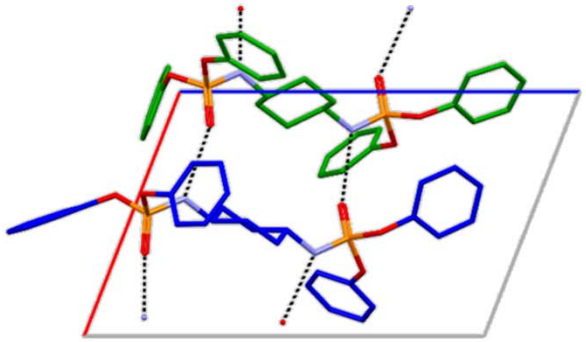
Approximate inversion symmetry would relate the C_2H_4 and CMe_2 bridges of the [2.2.1] cages but it seems the best description

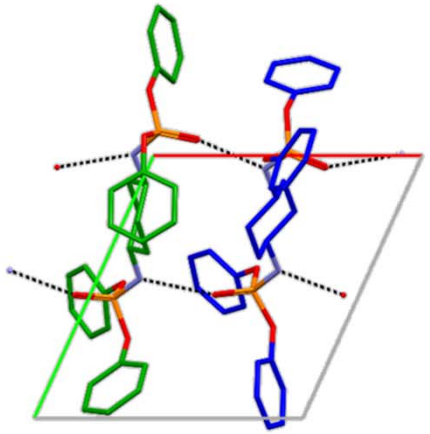
$P\bar{1}$ mimic or approximate translation [100]/2?

YIKWAT
(*P*1, *Z*=2)

Views along **a**, **b**, and **c**







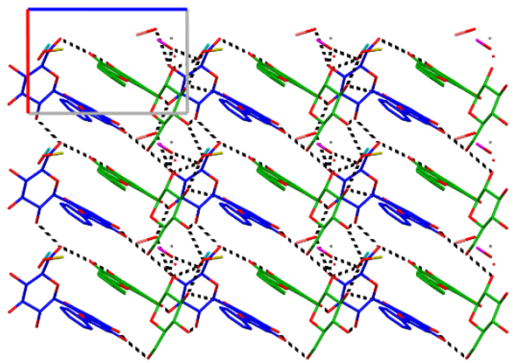
(molecules could have inversion symmetry but do not)

Description as having an approximate translation is marginally more convincing than description as a $P\bar{1}$ mimic

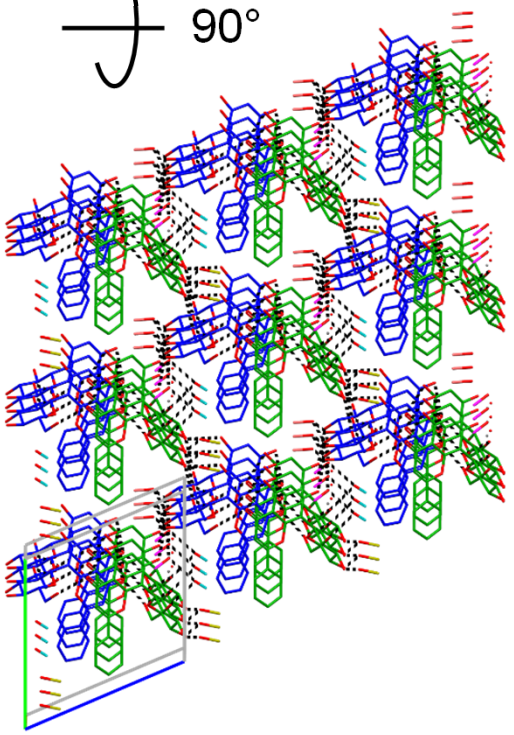
very distorted, but still easily recognizable, *C*2

YULFIV
(*P*1, *Z*=2)

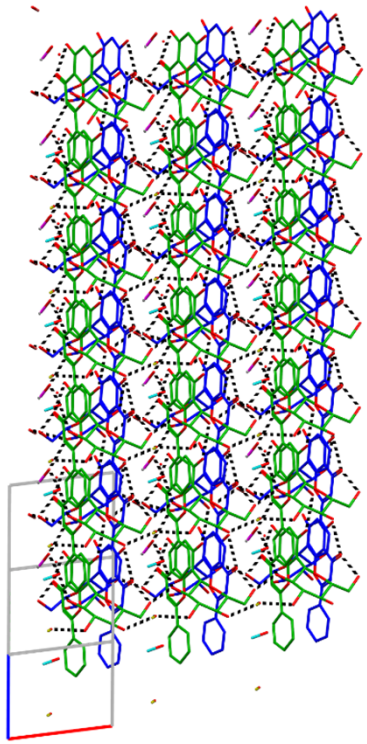
view along [010]



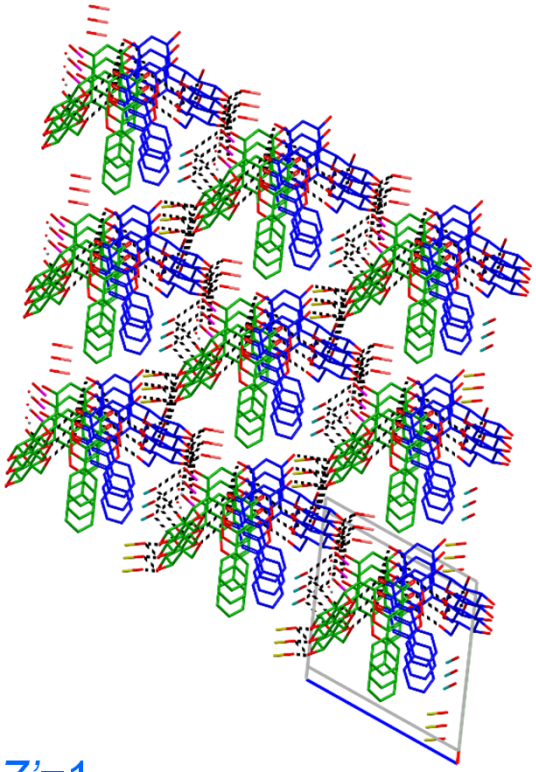
90°



view along [01$\bar{2}$]



90°

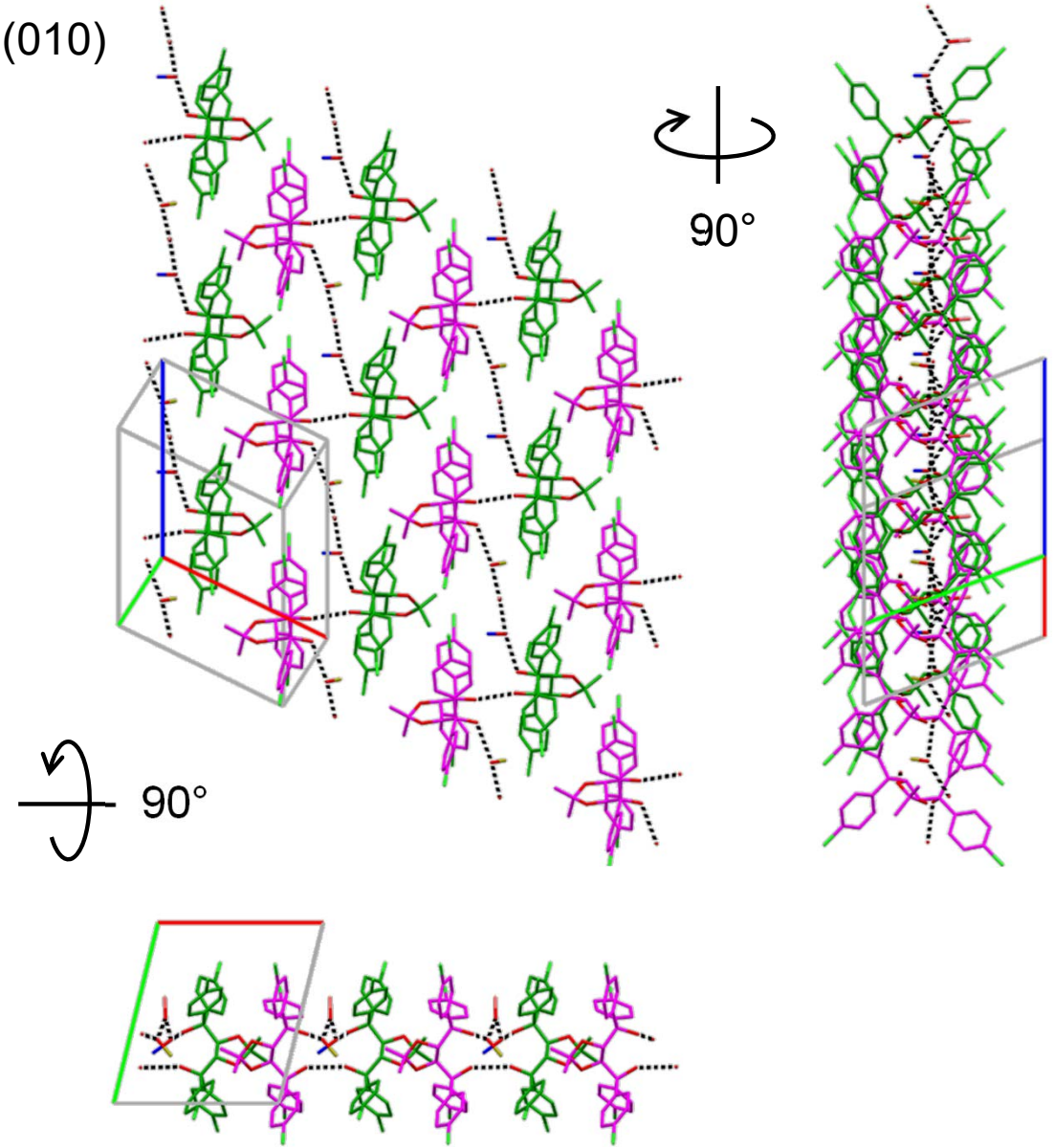


*C*2, *Z*=4, *Z'*=1
axes [01$\bar{2}$], [010], [100];
angles 82.4, 89.3, and 83.8°
α and γ are quite far from 90°
but the approximate 3-D
symmetry is obvious

borderline 2&2(1) (*c*211), 2-D

EABHIY
(*P*1, *Z*=2)

Layer (010)



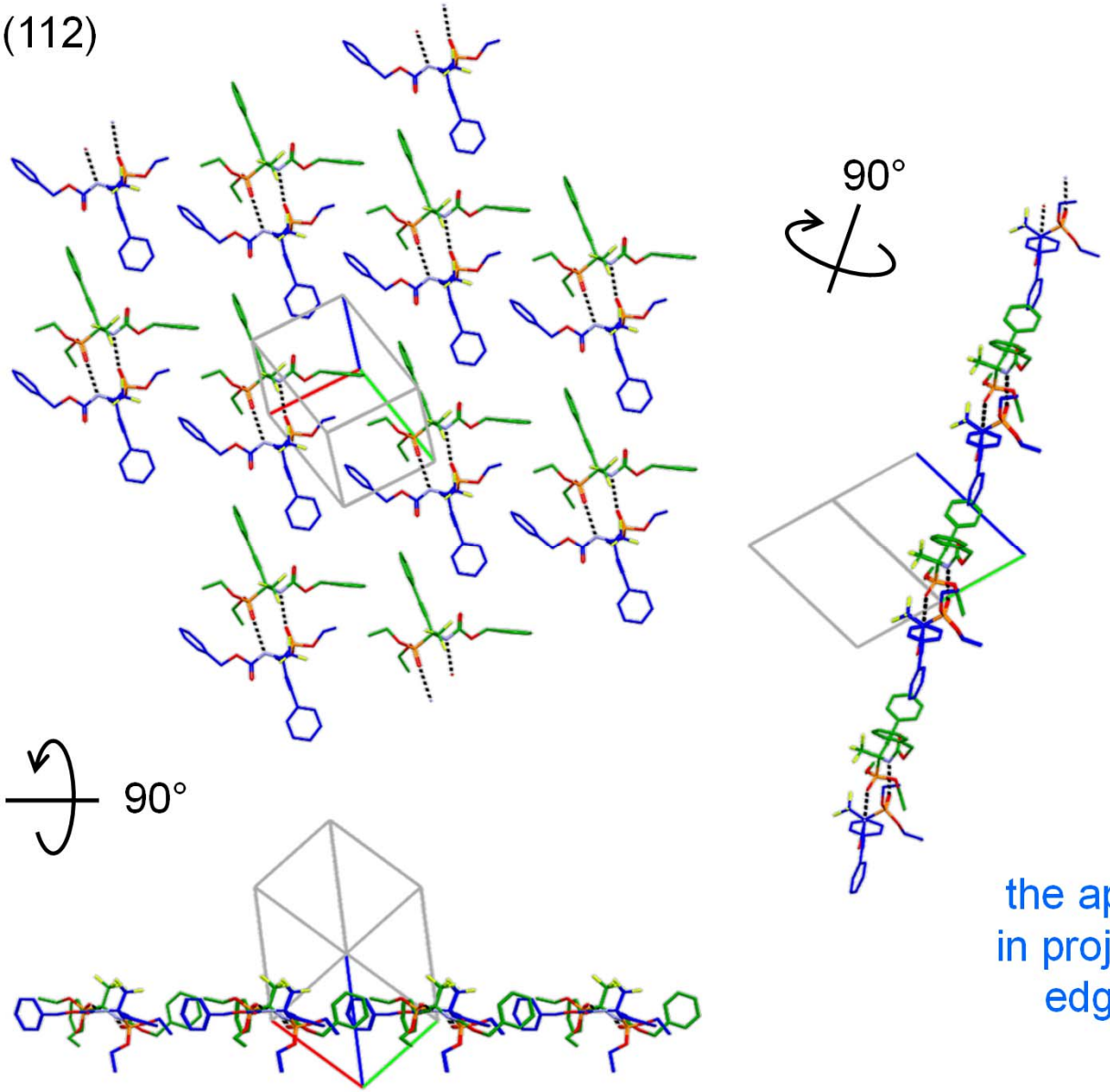
Layer (010)
*c*211, *z*=4, *z'*=1
axes [001], [201],
angle 96.2°

The MeOH molecules (3 for every large molecule) break the approximate symmetry and the layer angle is quite far from 90° but the approximate symmetry is obvious

*p*112 (2-D)?

EMEMUG
(*P*1, *Z*=2)

Layer (112)

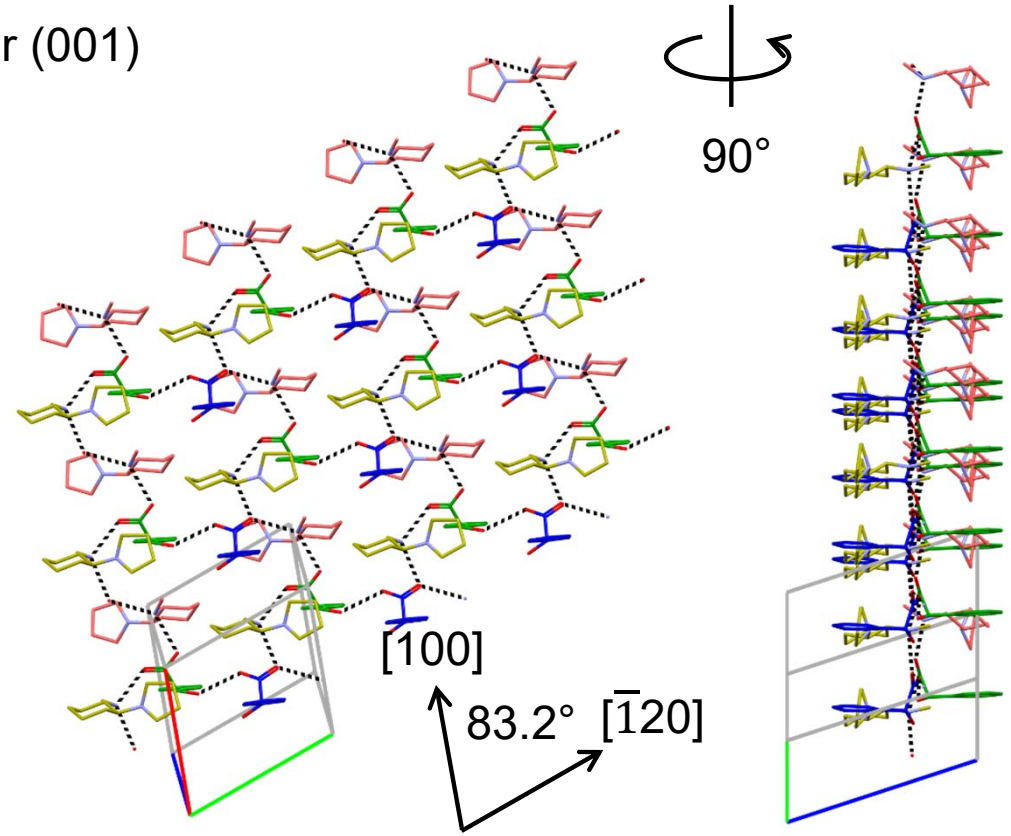


*p*112, *Z*=2, *Z'*=1
axes [1$\bar{1}$0], [11$\bar{1}$]
but
the approximate 2s look better in projection along (112) than in edge-on views of the layer

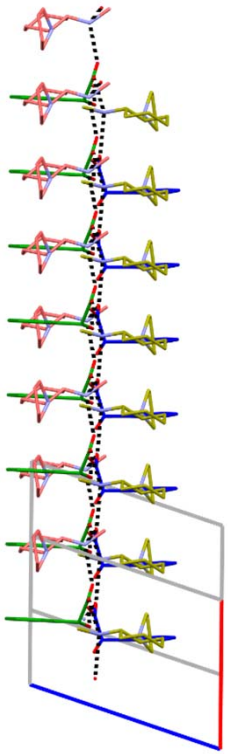
borderline 2&2(1) (*c*211), 2-D

FOYZUO
(*P*1, *Z*=4)

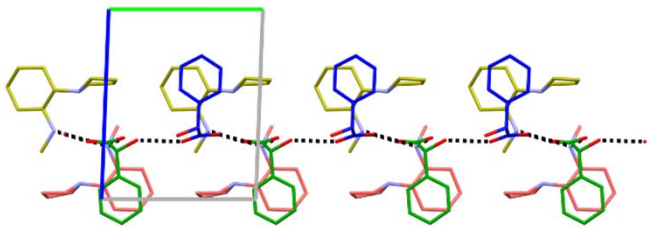
Layer (001)



View along [$\bar{1}$20]



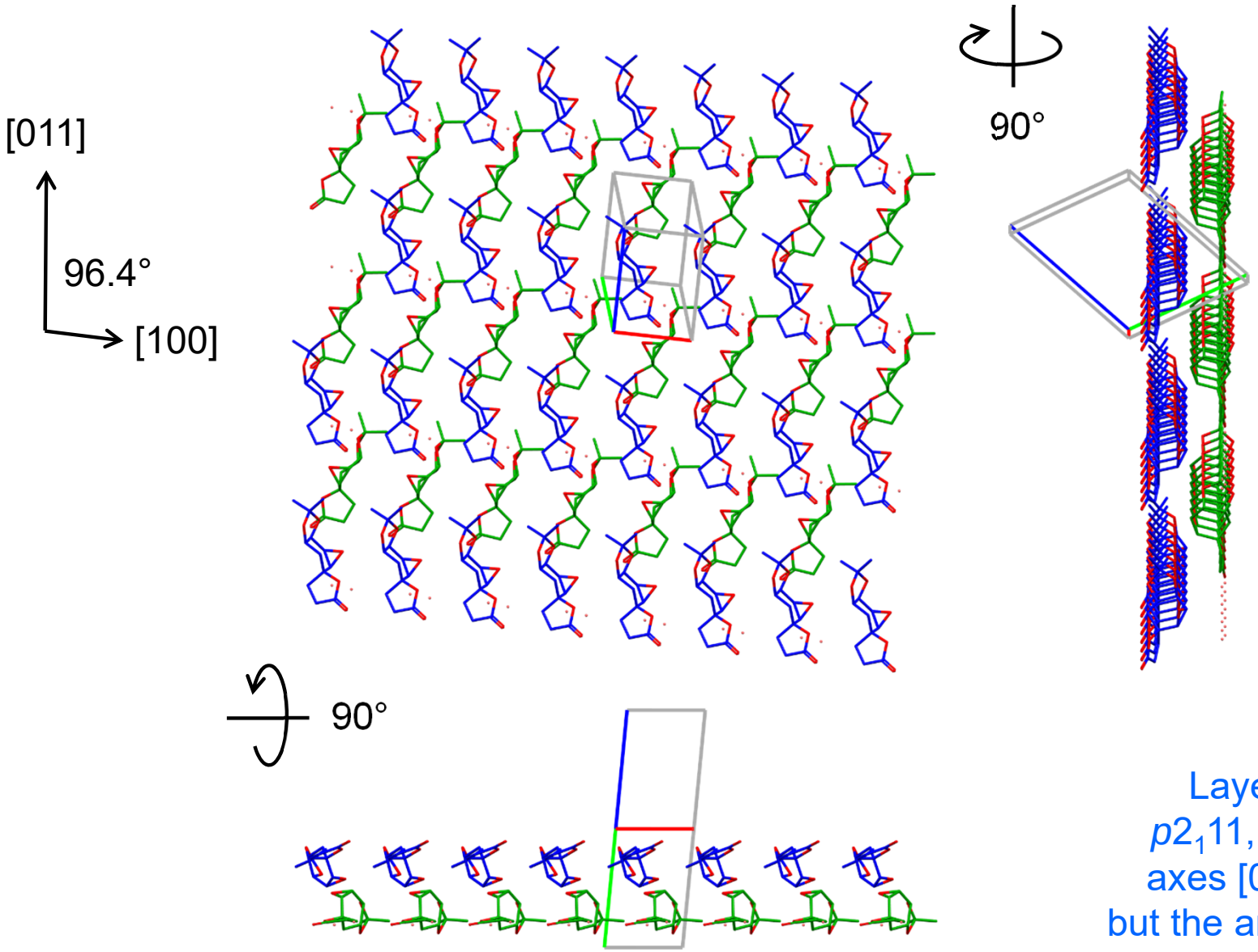
View along
[100]



borderline 2(1) ($p2_111$), 2-D

HIBTES
($P1$, Z=2)

Layer ($01\bar{1}$)

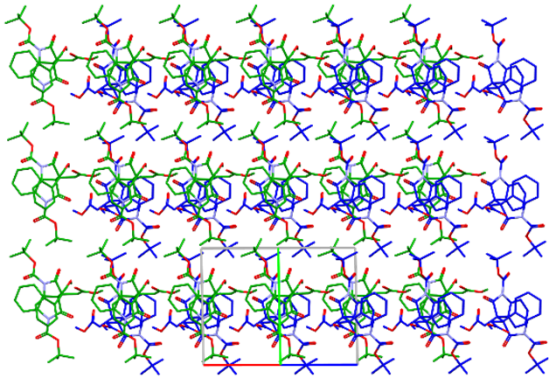


Layer ($01\bar{1}$)
$p2_111$, z=2, z'=1
axes [011], [100]
but the angle is 96.4°

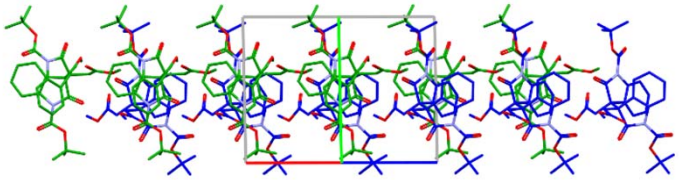
borderline 2&2(1) (*c*211), 2-D

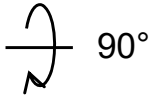
IDUYAK
(*P*1, *Z*=2)

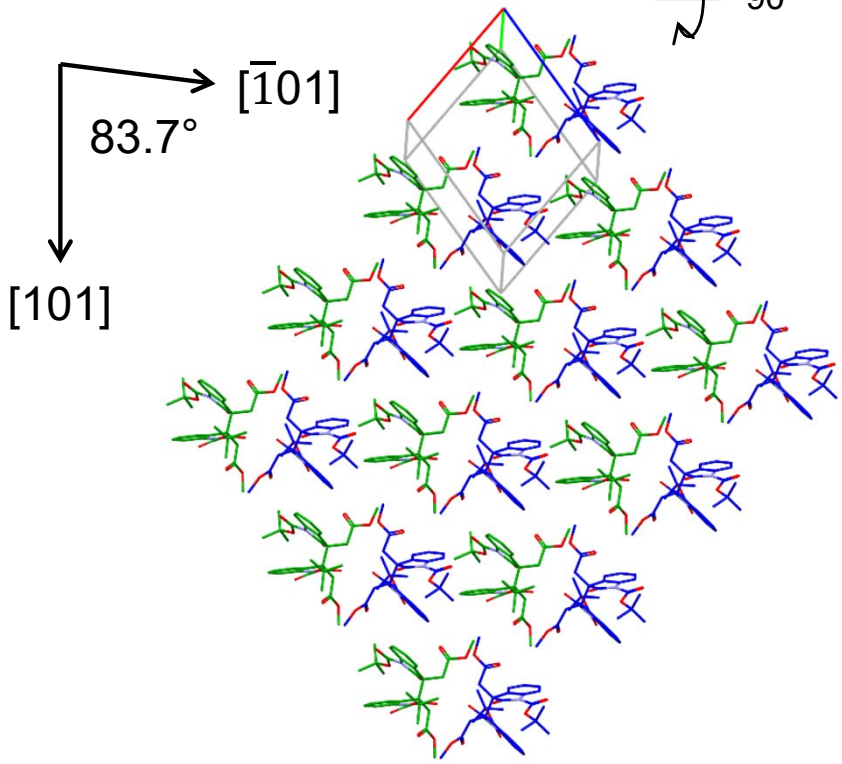
View along [101]
of layers (010)



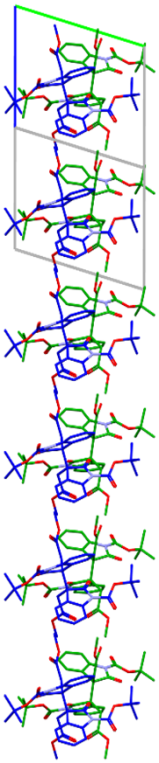
View along
[101] of a layer
(010)







View along [$\bar{1}$01]
of a layer (010)

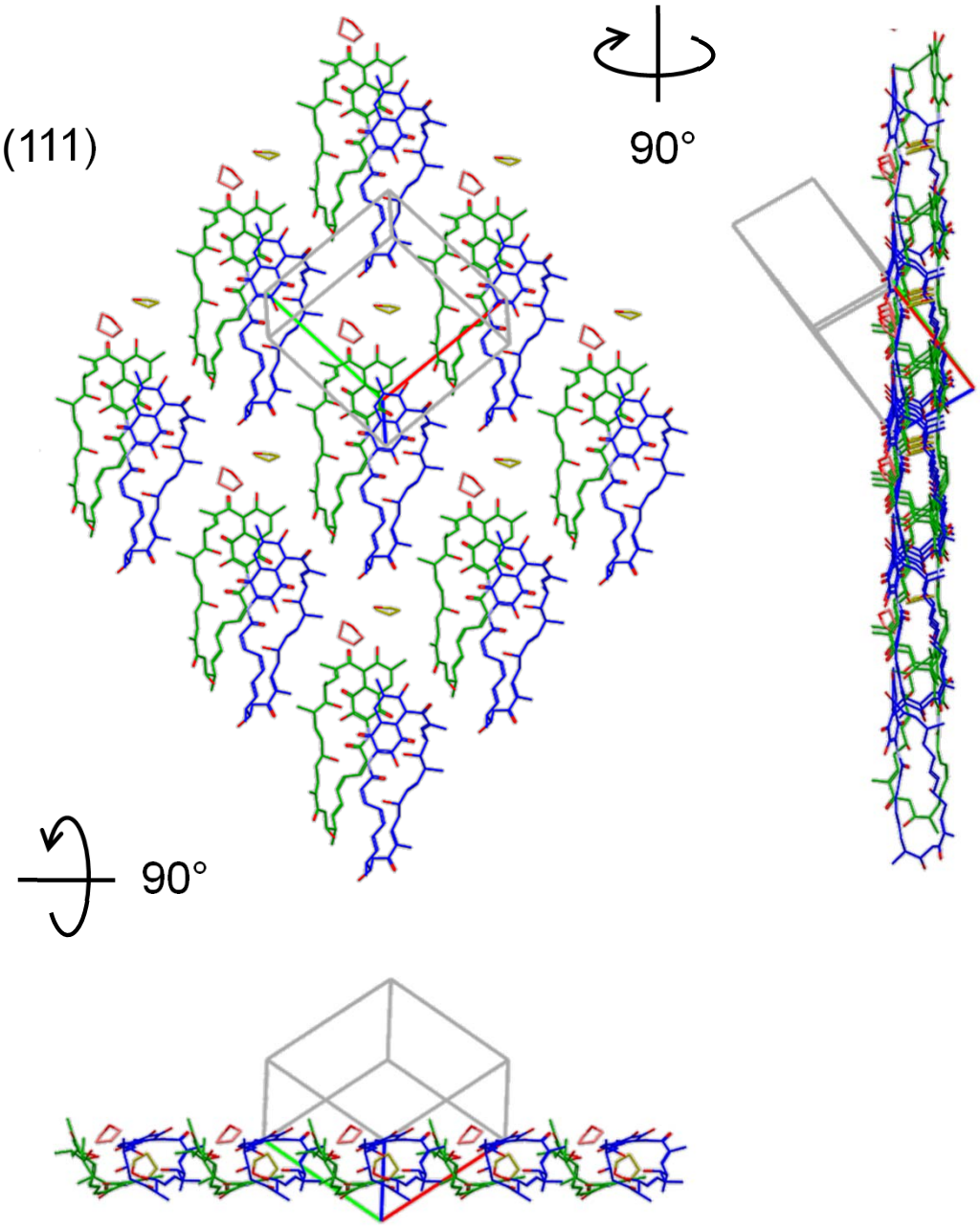


Layer (010)
*c*211, *z*=2, *z'*=1
axes [101], [$\bar{1}$01],
but the angle is 83.7°
and the approximate twofold
axes are rotated by 16° away
from [101]

borderline 2&2(1) (*c*211), 2-D

JIRDAP
(*P*1, *Z*=2)

Layer (111)

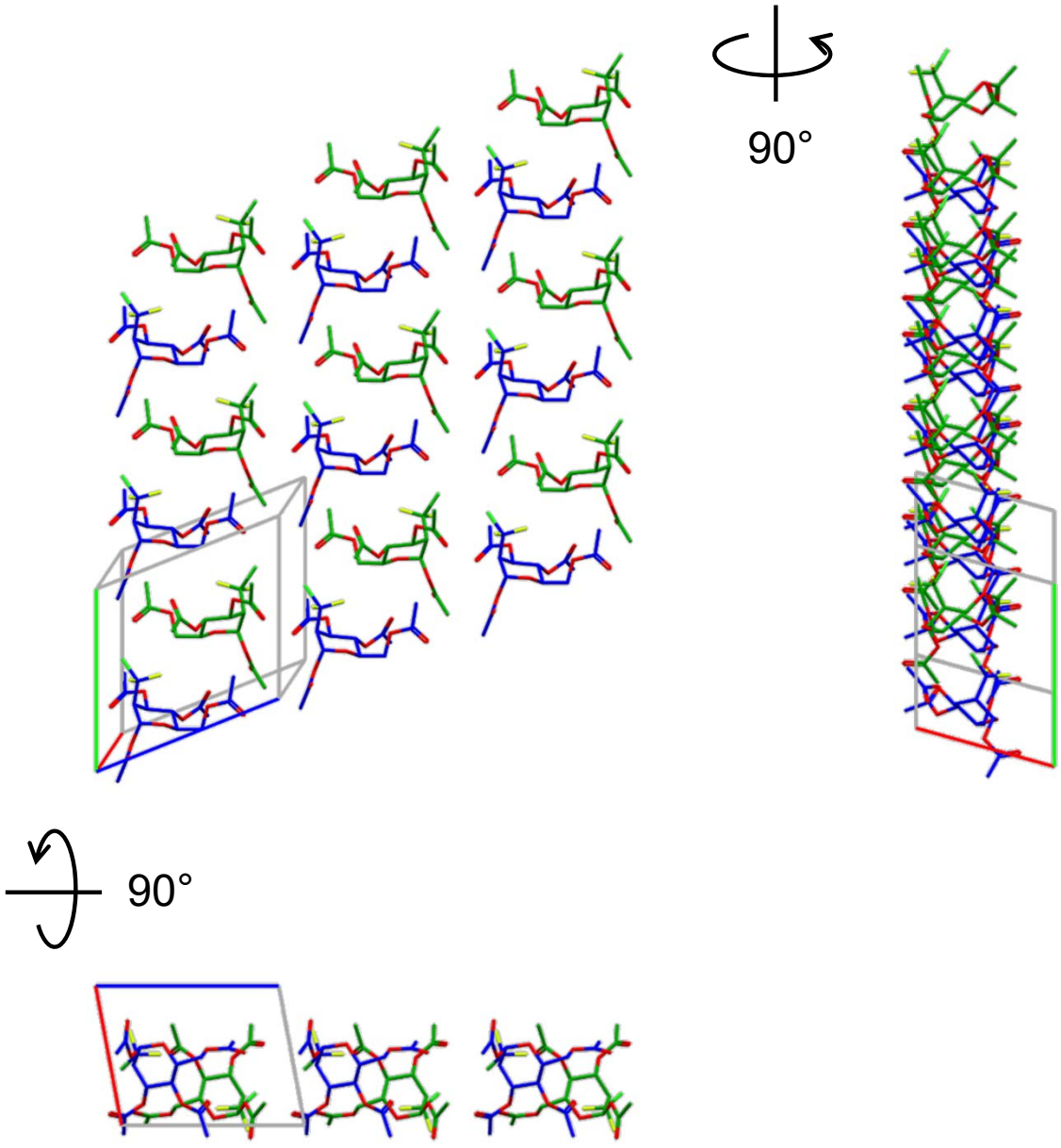


Layer (010)
*c*211, *z*=4, *z'*=1
axes [$11\bar{2}$], [$1\bar{1}0$],
angle 91.4°
but
the molecules are not at
quite the same place
along the twofold axis

2&2$_1$, 2-D?

NADREQ
(*P*1, *Z*=1)

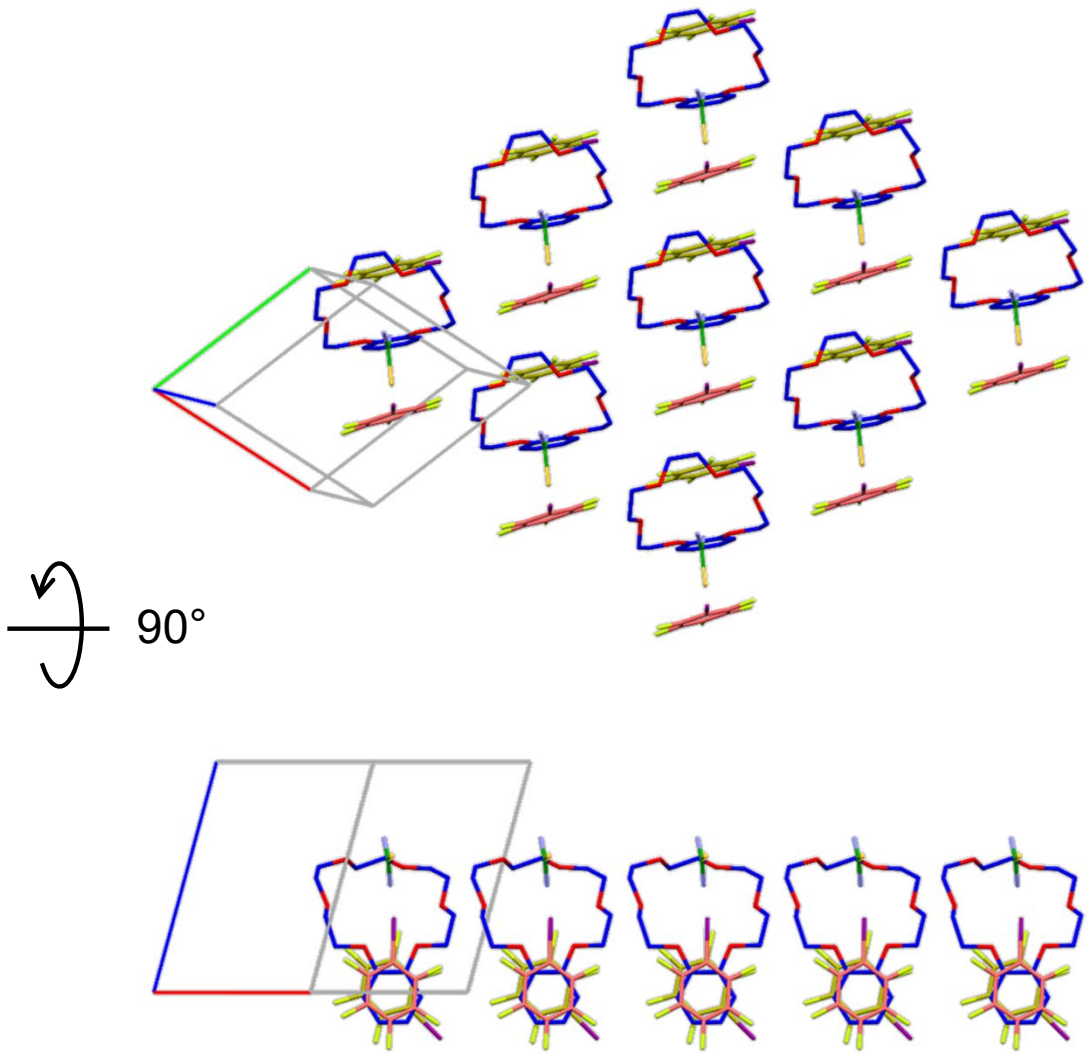
Layer (100)



Layer (100)
*c*211, *z*=4, *z'*=1
axes [010], [0$\bar{1}$2];
but the angle is 95.7°
and
the twofold requires a
small translation along **b**

distorted higher symmetry (*cm*11), 2-D? (achiral)

OQIJEF
(*P*1, *Z*=1)



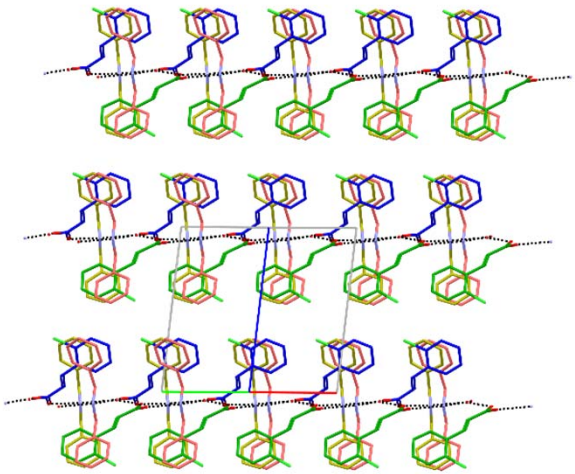
very distorted *cm*,
z=2, *z'*=½
axes [110], [1$\bar{1}$0];
the angle is 93.7°
but
the mirror symmetry is
not very good

borderline 2&2(1) (*c*211), 2-D

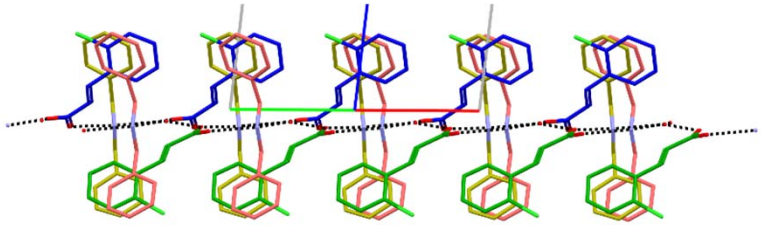
PEQGAU
(*P*1, *Z*=2)

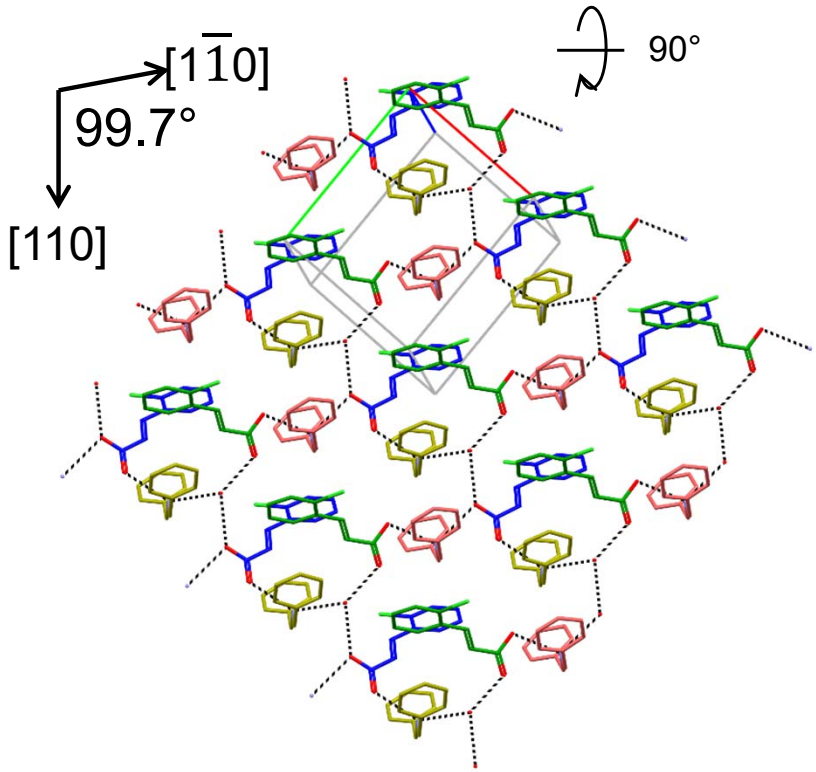
(a 1:1:½ salt hydrate)

View along [110] of layers (001)

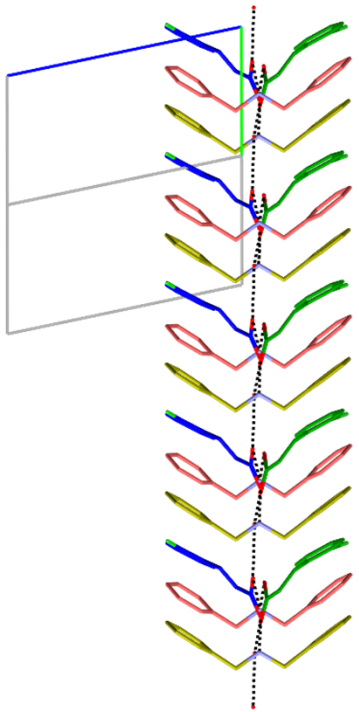


View along [110] of a layer (001)





View along [1$\bar{1}$ 0] of a layer (001)



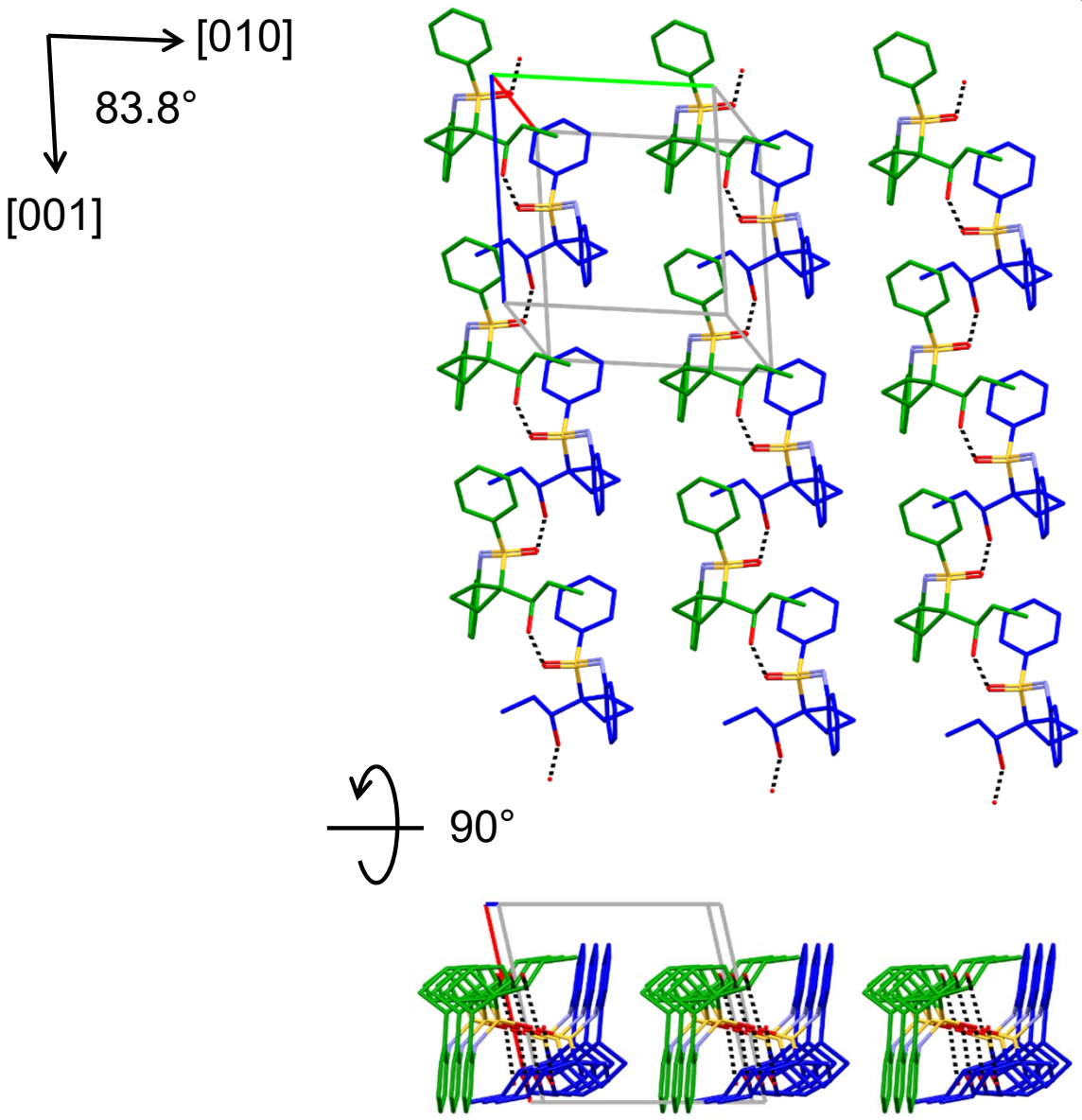
Layer (001), *c*211, *z*=2, *z'*=1
axes [110], [1$\bar{1}$0],
but the angle is 99.7°

The anion lies on a general position but each of the two cations lies on an approximate twofold axis. The one H_2O breaks the approximate *c*211 symmetry

borderline 2(1) ($p2_111$), 2-D

PIVZAW
($P1$, Z=2)

Layer (100)

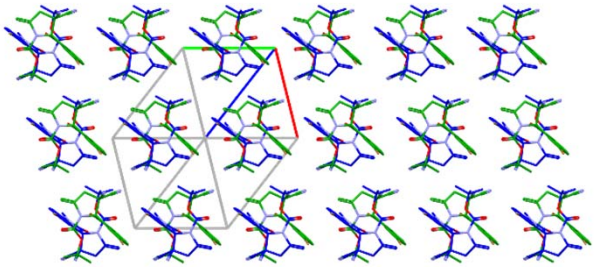


Layer (100)
$c211$, z=2, z'=1
axes [001], [010]
but the angle is 83.7°

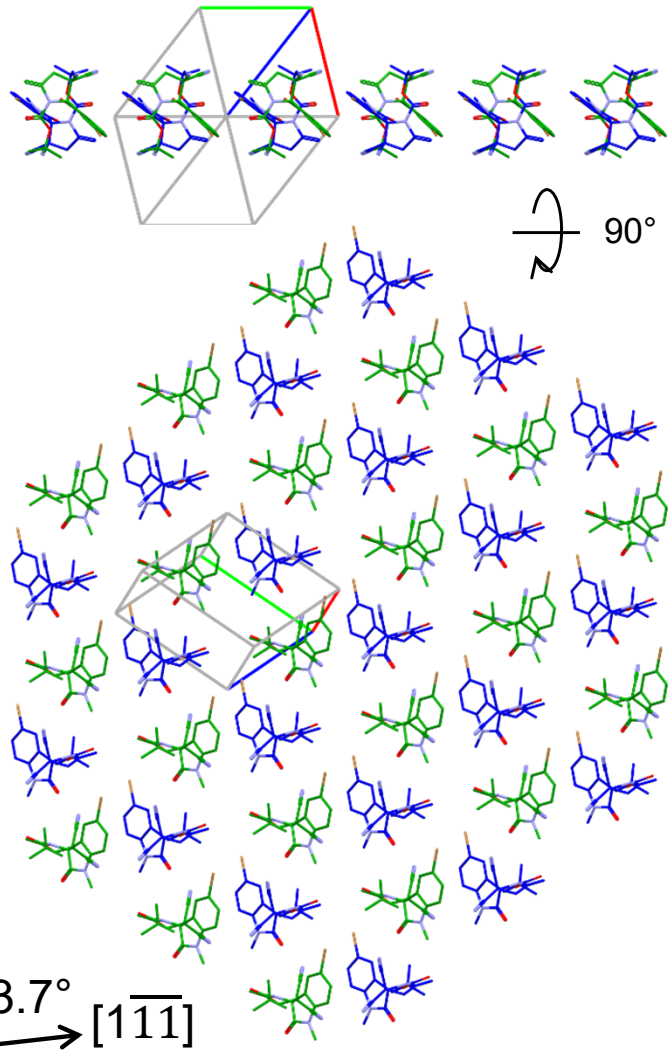
borderline 2&2(1) (*c*211), 2-D

SEYNOB
(*P*1, *Z*=2)

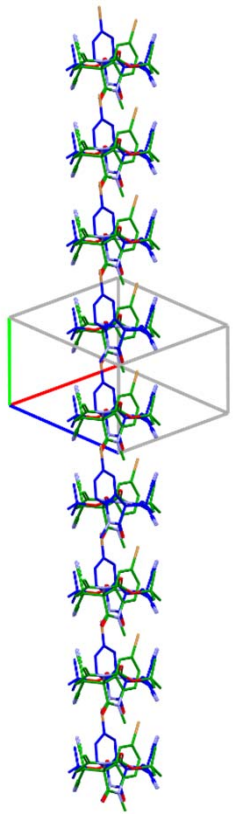
View along $[11\bar{1}]$
of layers (101)



View along
$[11\bar{1}]$ of a layer
(101)



View along $[1\bar{1}\bar{1}]$
of a layer (101)

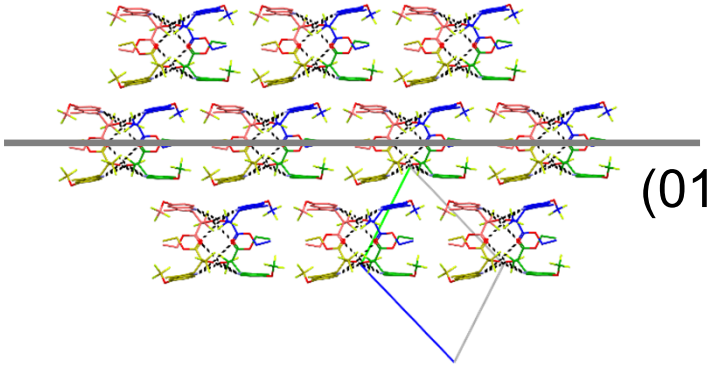


Layer (101)
*c*211, *z*=2, *z'*=1
axes $[11\bar{1}]$, $[1\bar{1}\bar{1}]$
but the angle is 83.7°

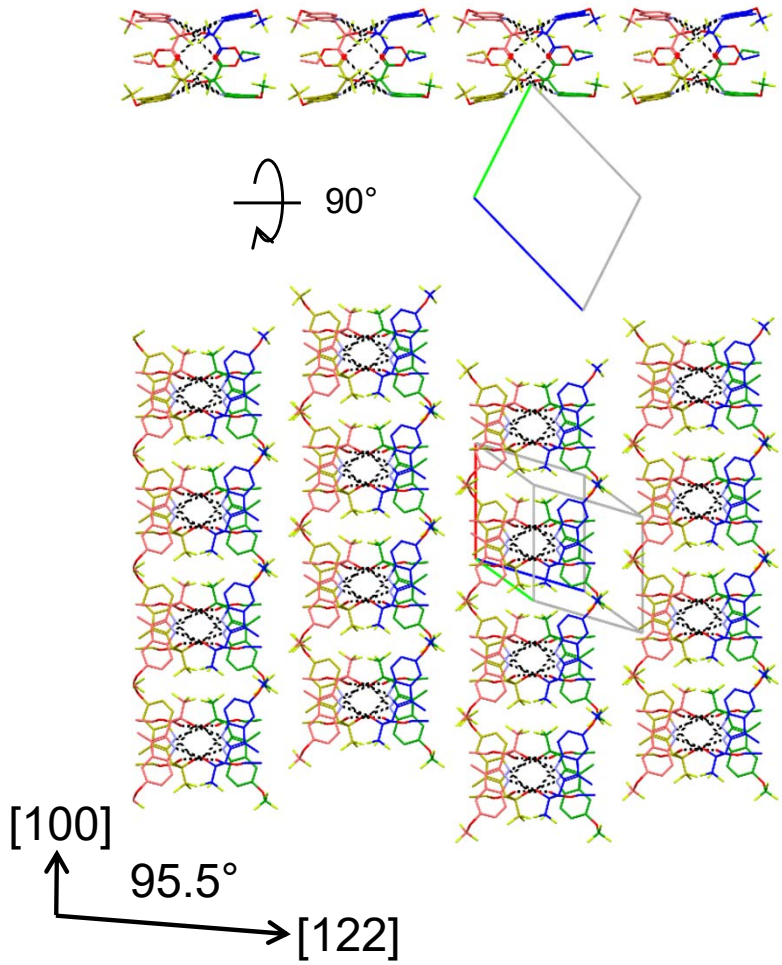
222 (*c*222), 2-D

SOXMAW
(*P*1, *Z*=4)

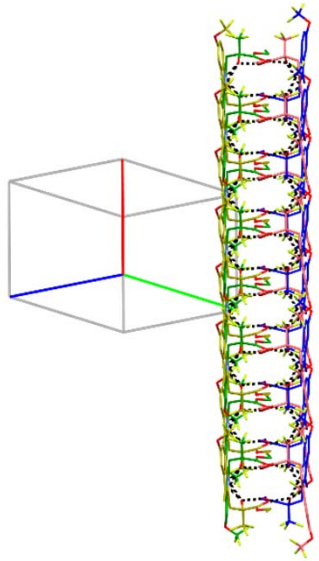
View along [100]
of layers $(01\bar{1})$



View along
[100] of a layer
$(01\bar{1})$



View along
[122] of a layer
$(01\bar{1})$



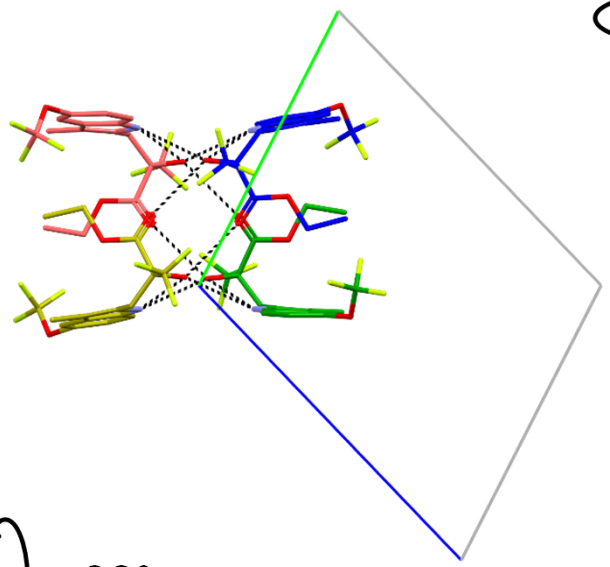
Layer $(01\bar{1})$
*c*222, *z*=4, *z'*=1
axes [100], [122],
but the angle is 95.5°

(see also next page)

222 (*c*222), 2-D

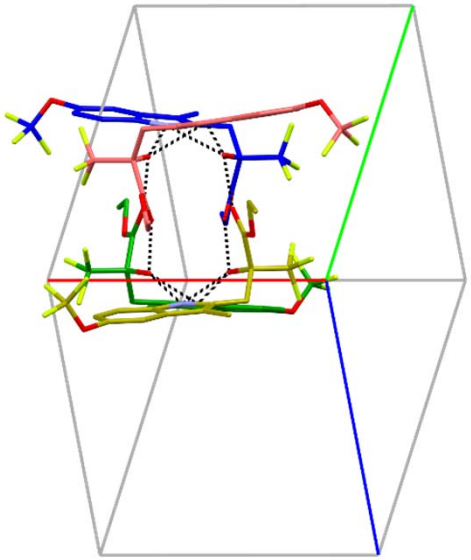
SOXMAW, con't (*P*1, *Z*=4)

View along [100]

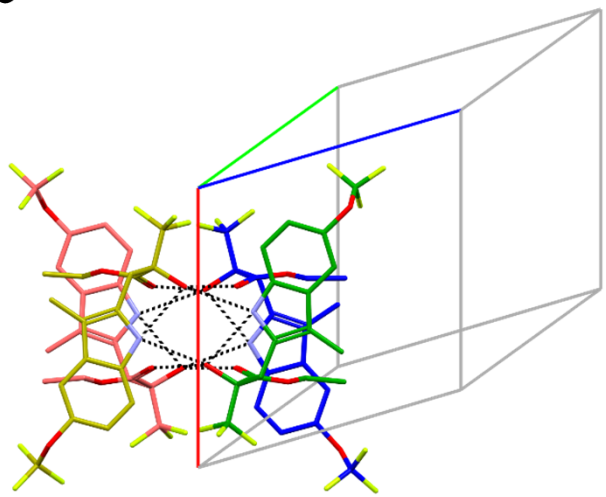


95.5°

View along [122]



90°

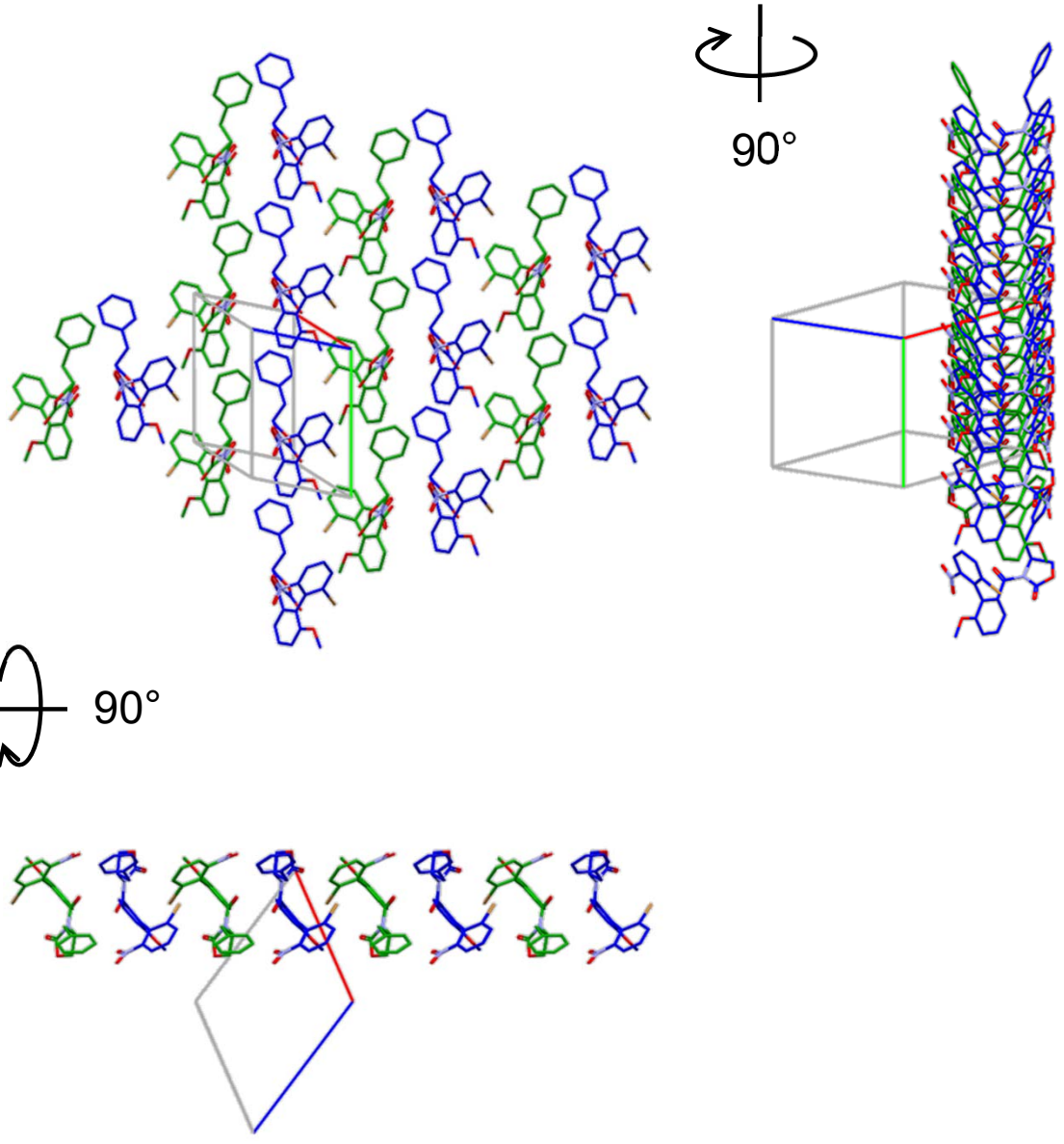


The H-bonded unit has approximate symmetry 222

2&2$_1$, 2-D?

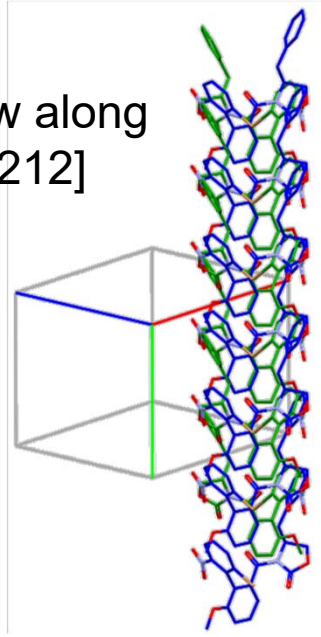
XIKMAG
(*P*1, *Z*=2)

Layer (10$\bar{1}$)



Layer (10$\bar{1}$)
*c*211, *z*=4, *z'*=1
axes [010], [212];
but the angle is 83.2°
but
the approximate 2 and 2$_1$ axes along **b** are quite obvious

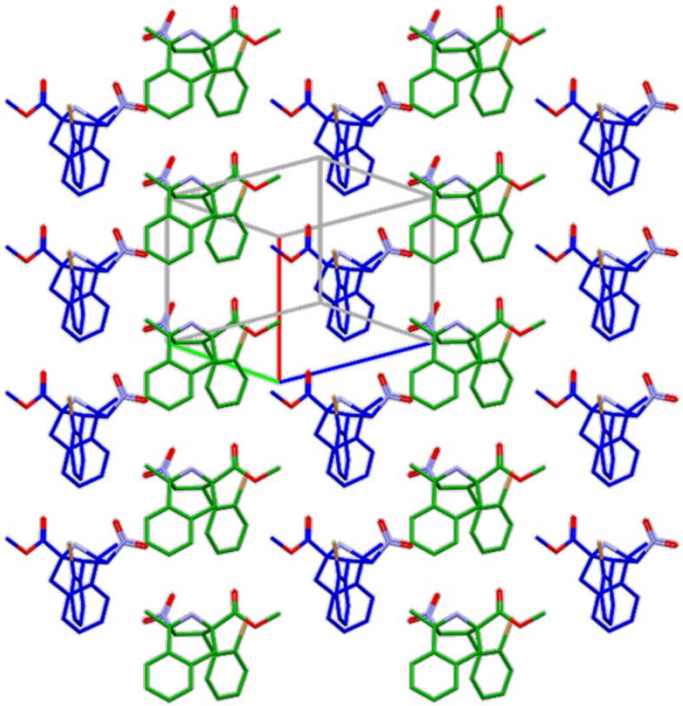
View along [212]



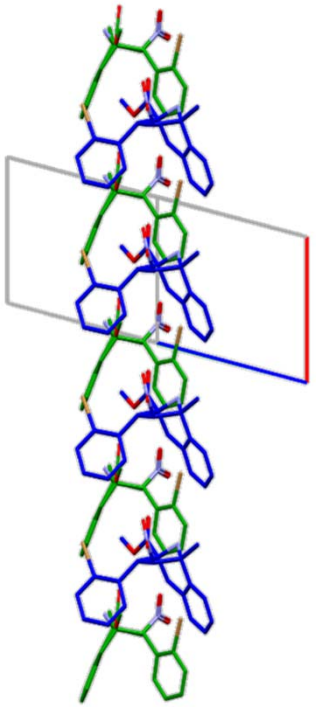
$p2_111$ (2-D)?

XITGAK
(*P*1, *Z*=2)

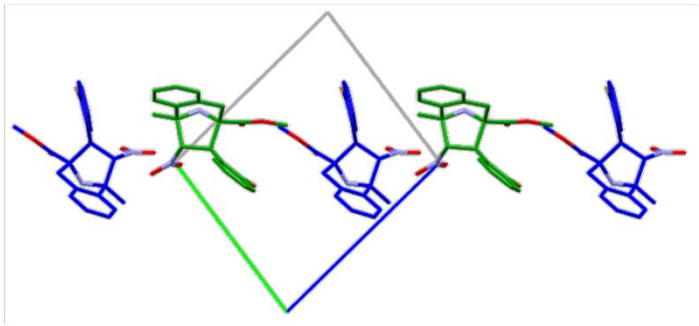
Layer (011)



90°



90°

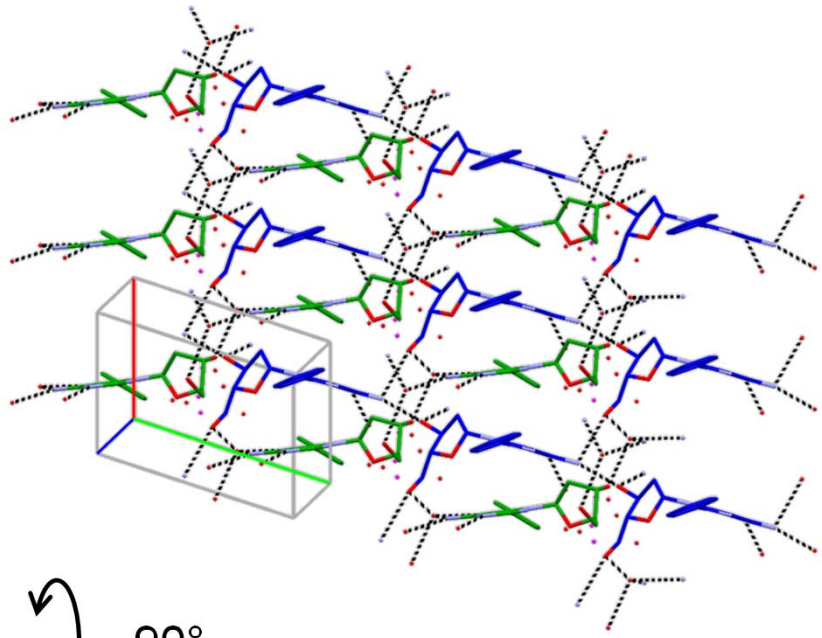


$p2_122$, Z=2, Z'=1
axes [100], [$01\bar{1}$];
angles 90.1°
but
the orientations of the molecules
aren't quite right

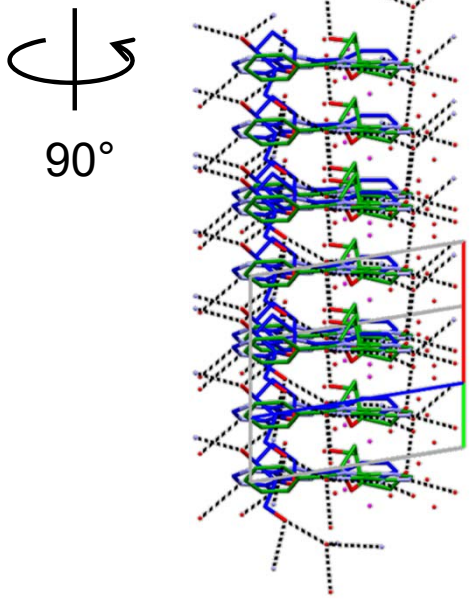
borderline 2&2(1) (*c*211), 2-D

XUQJOJ
(*P*1, *Z*=2)

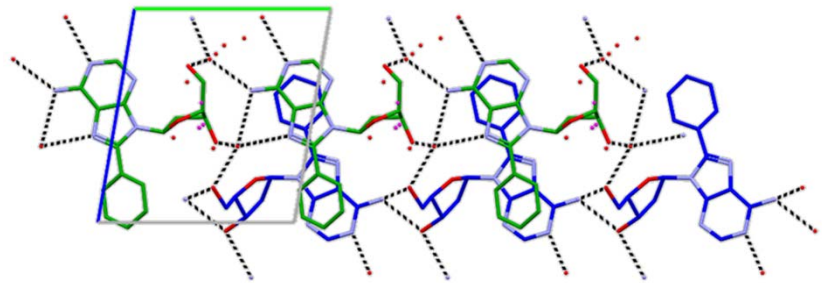
Layer (001)



90°



90°



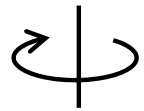
Layer (001)
*c*211, *z*=4, *z'*=1
axes [100], [120],
angle 88.2°

The approximate c211 symmetry is better for the planar adenine rings than for the deoxyribose fragments. and the layers are connected by H bonds

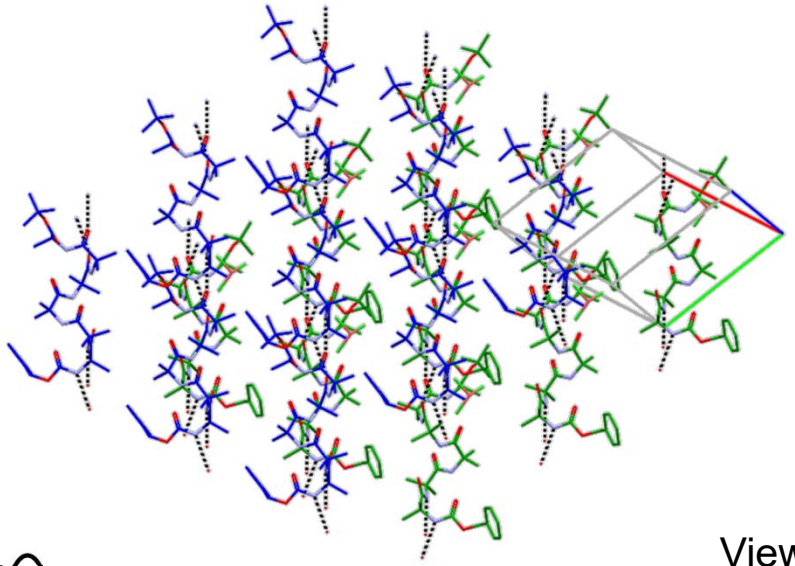
borderline 2&2(1) (*c*211), 2-D

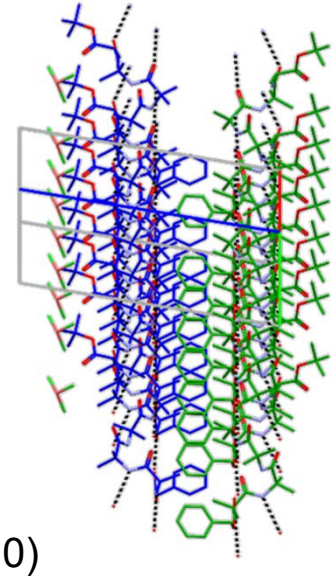
ZODHIL
(*P*1, *Z*=2)

Layer (001)

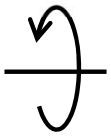


90°



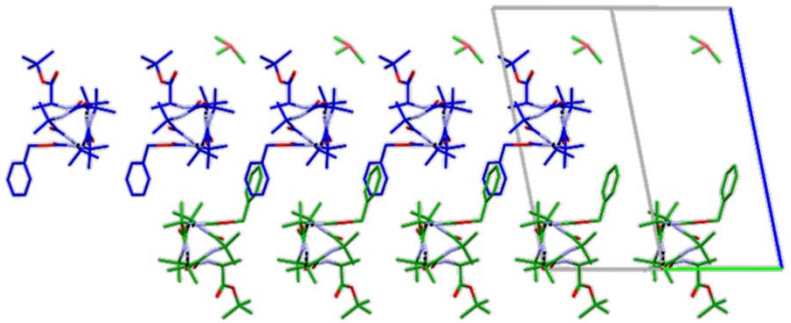


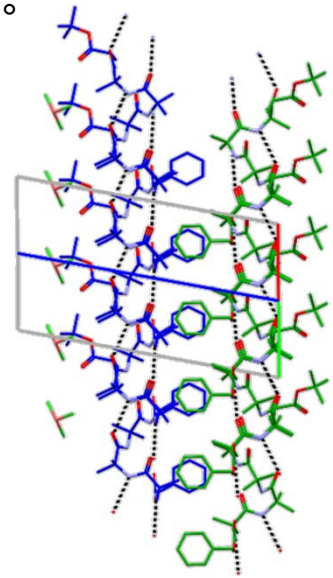
Layer (010)
*c*211, *z*=4, *z'*=1
axes [1$\bar{1}$0], [110],
angle 97.8°



90°

View along (110)
(rotated by 7.8°
from the view
above)



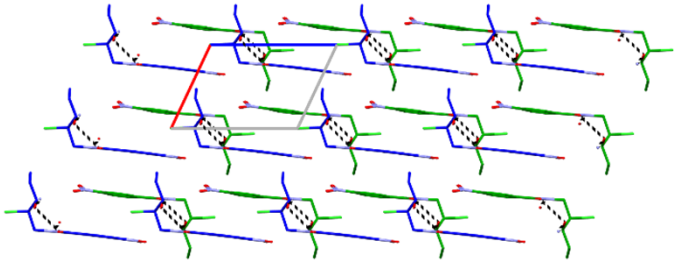


The angle of the
*c*211 cell is quite
far from 90° but
the approximate
symmetry is
obvious

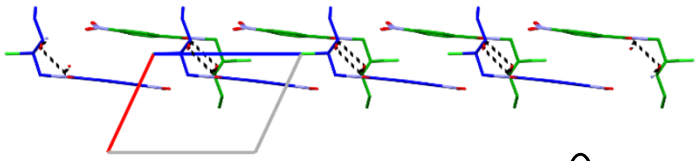
borderline 2&2(1) (*c*211), 2-D

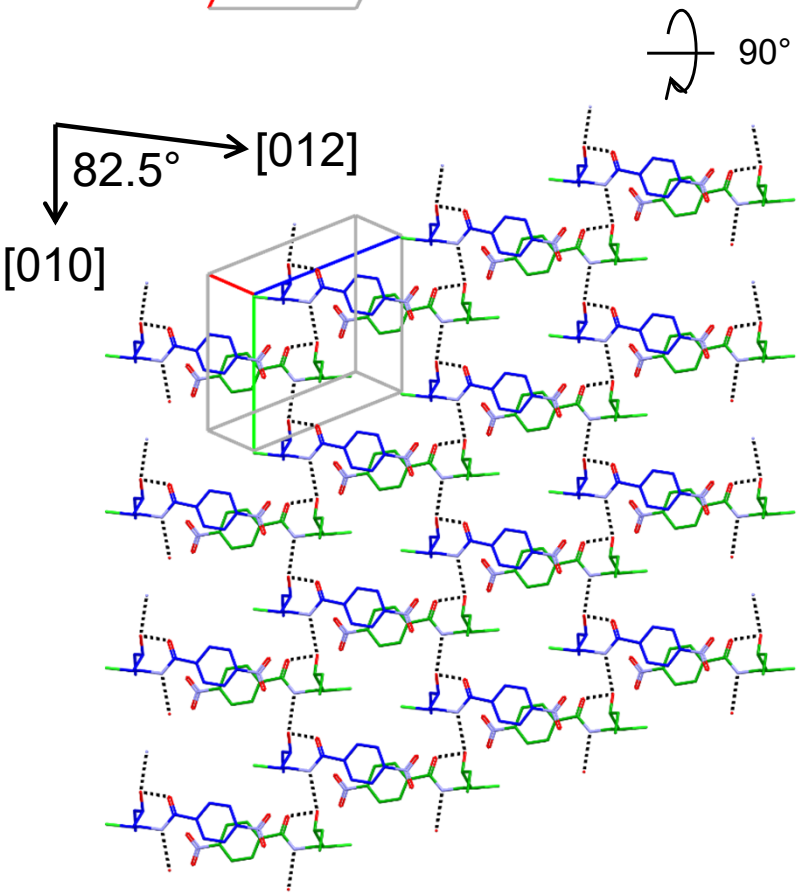
ZUWDIG
(*P*1, *Z*=2)

View along [010]
of layers (100)

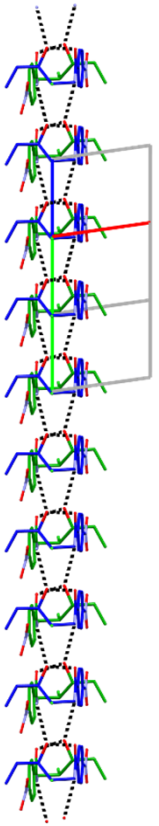


View along
[010] of a layer
(100)





View along [012]
of a layer (100)



Layer (100)
*c*211, *z*=2, *z'*=1
axes [010], [012],
but the angle is 82.5°