Diffraction Methods in Undergraduate Education

Teaching Crystallography to Chemists in the CCD Era

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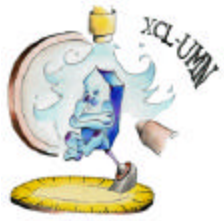
Goals

- X-Ray crystallography course design, expectations, needs, and wishes
- Resources for twins and twinning
- Some properties of twins
- Non-merohedral twin example of simple-to-grow materials
- Pseudo-merohedral twin example of simple-to-grow materials
- Final thoughts

XCL-UMN Timeline



- 1995 – UMN obtained first CCD diffractometer.
- 1998 - Faculty member who taught crystallography course retired.
- 1999 - Obtained second CCD diffractometer. It was purchased with the intent that it would be used primarily to train students in the crystallography course and secondarily for trained users to collect their own data.
- 1999 – 2001 – The X-Ray Crystallography course attracts 10 students on average per year. About one-half make use of their training in their graduate research. Some undergraduates have attended.

Traditional X-Ray Crystallography Course

Strong Emphasis	**Weak Emphasis**
Symmetry	Literature
Space groups	Laboratory methods
Diffraction theory	Statistics
Structure factors	Disorder
Fourier methods	*Twinning*
Thermal motion	Pseudosymmetry
Anomalous scattering	Publication of results
Derived results	Other diffraction methods

New X-Ray Crystallography Course Design

- The focal point of the course is the final project where the student chooses a material with an unknown structure, independently collects data and solves structure, and makes a presentation to the class.
- Streamline materials to focus instruction around the most common space groups.
- 11 of the first 15 weeks have laboratory assignments that progressively prepare them for the final project.
- About one-third the structures pose some experimental or crystallographic problem that the entire class benefits from seeing explained.

What Everyone Wants

- **Chemistry Professors –** Desire to have their graduate and postdoctoral students collect data, solve and refine structures efficiently, prepare publication materials and *get back into the lab* to do it again.
- **Graduate Students –** Would prefer to be trained by a senior graduate student, but we require the completed class.
- **Postdoctoral Students –** Want run of the laboratory whenever they please.
- **XCL Director –** Attempts to keep everything running efficiently and everyone happy.

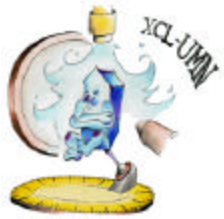
Teaching Wish List

- A single textbook that serves all of my needs.
- Better tools to demonstrate what direct methods do to solve crystal structures.
- Better graphical methods to demonstrate the relationships between the direct- and reciprocal space.
- Better graphical methods to illustrate how all atoms in the unit cell contribute to a particular structure factor.

Resources for Twinning on the Web: Tools to Integrate in Teaching Crystallography

- http://shelx.uni-ac.gwdg.de/~rherbst – Regine Herbst-Irmer has three completely worked examples of merohedral, pseudo-merohedral, and reticular pseudo-merohedral twinning. A step-by-step presentation *with data* is available for each example.
- http://www.doe-mbi.ucla.edu/Services/Twinning/ - Tod Yates and Barry Fam operate a detwinning service for proteins.
- http://mineral.galleries.com/minerals/property/twins.htm - A collection of mineral twins is presented by Amethyst Galleries, Inc.
- http://www.ccp4.ac.uk/dist/ccp4i/help/modules/appendices/twinning.html - CCP4 graphical user interface for twinning.
- http://www.xtl.ox.ac.uk/twin.html- David Watkin has very useful information about various twins, how to determine the proper twin law, references on refinement, plus some examples.

The Many Flavors of Twinning



- **Merohedral twins -** The lattices of all twin components coincide perfectly in both direct *and* reciprocal space. 159 of the 230 space groups belong to merohedral point groups.
- **Pseudo-merohedral twins -** Common examples are monoclinics with $\beta \sim 90.0°$ or $a \sim c$ with $\beta \sim 120.0°$. These can often be treated properly once the structure is solved. The correct twin law is usually related to the additional symmetry gained.
- **Reticular pseudo-merohedral (Chameleon) twins -** Subclass of non-merohedral twins that emulate higher, usually centered crystal systems.
- **Non-merohedral twins -** Some axes coincide in reciprocal space, but others do not. Therefore part of the reciprocal lattice is exactly overlapped while other parts are not. The phenomenon of partially overlapping reflections is a serious problem.

Warning Signs of a Non-Merohedral Twin

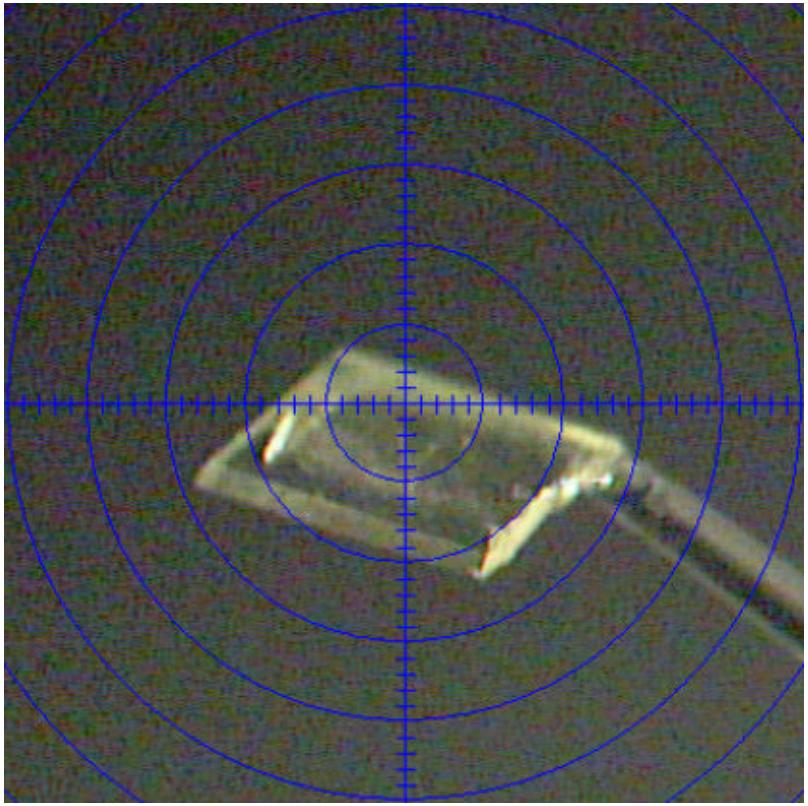
- The specimen may not index easily with the standard software. If it does index, then many reflections do not fit the cell. The reflections that do not index may have 1 or 2 non-integer *h*, *k*, *l* indices.
- The specimen may index, but based on chemical knowledge it appears to have a unit cell with an unexpectedly large volume. The expected Z is likely too large based on the maximum number for the crystal system.
- The unit cell has a sensible volume, but Laue symmetry is not confirmed in the initial analysis; twinning can make the Rint much greater than the final R1.
- The reflection statistic $|E^2-1|$ value is shifted to a lower value when twins have frequent overlap: centrosymmetric ~ 0.8 and non-centrosymmetric ~0.6.
- The worst fitting reflections have $Fo^2 >> Fc^2$ and usually have a systematic trend in some or combined indices of *h*, *k*, and or *l*.

Source: R. Herbst-Irmer and G Sheldrick, *Acta Cryst.* B**54**, 443 (1998)

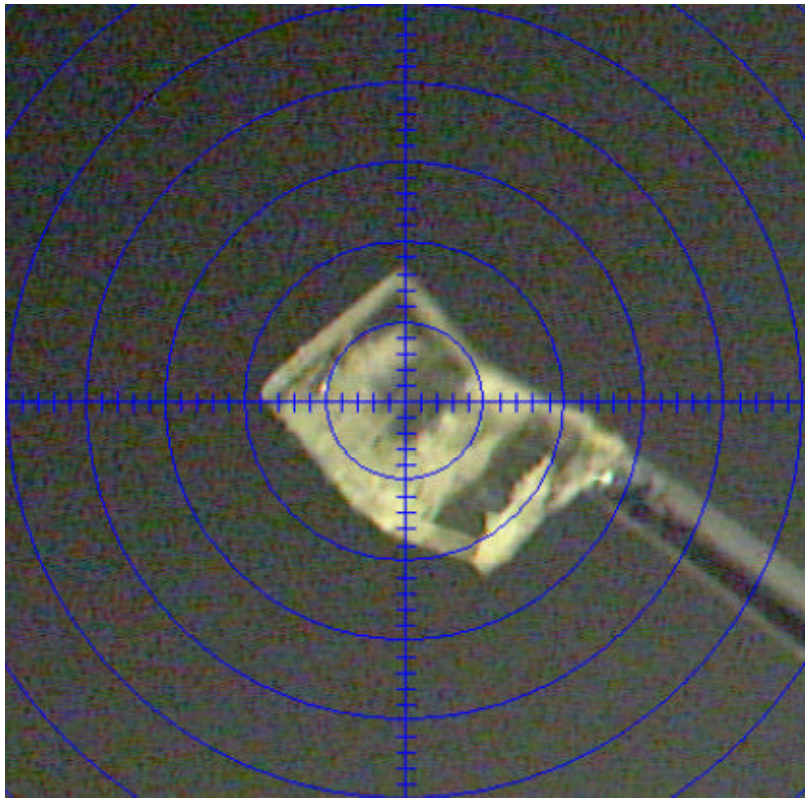
Twinning in 2,3,5,6-Tetrachloro-1,4-bis(cyano)benzene hexamethylbenzene clathrate

The specimen undergoes a phase change to a non-merohedral twin in triclinic and folds in “V” shape

Polymorph 1: 298 K, *C*2/m



Polymorph 2: < 279 K, $P\bar{1}$



Source: D. Britton, private communication

A Dramatic Change in Color is Associated with $\{[HC(3,5\text{-}Me_2pz)_3]_2Fe\}[BF_4]_2$ Phase Transition

<204K: primitive triclinic, non-merohedral twin, color is deep purple

>204K: C-centered monoclinic, double volume, no color

Phase Transition with Onset of Non-Merohedral Twinning: An Example You Can Use in the Classroom and Lab

- 18-Crown-6 bis-(acetonitrile) clathrate is a simple crystal to grow for this demonstration. Dissolve 18-crown-6 in acetonitrile and chill in refrigerator. The specimens must be handled quickly or they will desolvate. Sub-ambient specimen transfer is recommended!
- We have confirmed that the structure is a non-merohedral twin below ~168 K. The phase transition is reversible going between monoclinic and triclinic phases.
- The phase transition is *reversible* without doing any damage to the specimen.
- The twin law corresponds to a 180º rotation of [100].

Phase Transition with onset of Non-Merohedral Twinning: An Example You Can Use in the Classroom and Lab

GEFREO

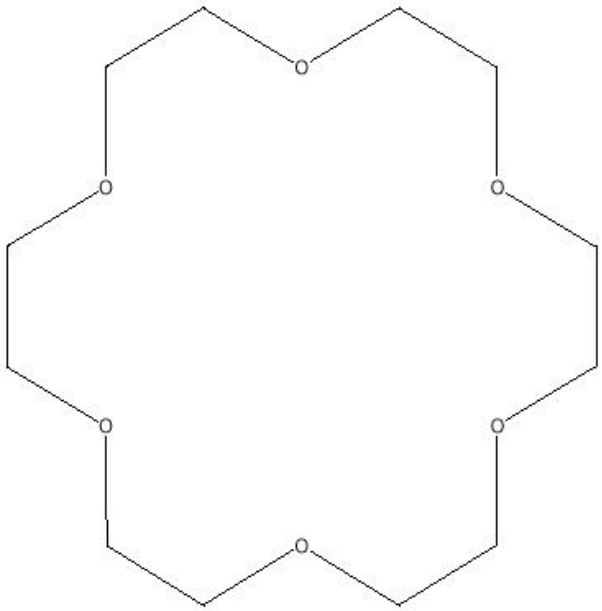
Reference: R.D.Rogers, P.D.Richards, E.J.Voss (1988) *J.Inclusion Phenom.Macrocyclic Chem.*,**6**,65

Formula: $C_{12}H_{24}O_6.2(C_2H_3N_1)$

Compound Name: 18-Crown-6 bis(acetonitrile) clathrate

Space Group:	P-1	***Cell:***	***a***	8.343(7)	***b***	8.982(4)	***c***	13.576(4)
Space Group No.:	2	***(Å,°)***	α	105.50(3)	β	91.80(8)	γ	91.28(9)

R-Factor (%): 10.3 ***Temperature(K):*** 123 ***Density(g/cm^3):*** 1.174



GEFREO01

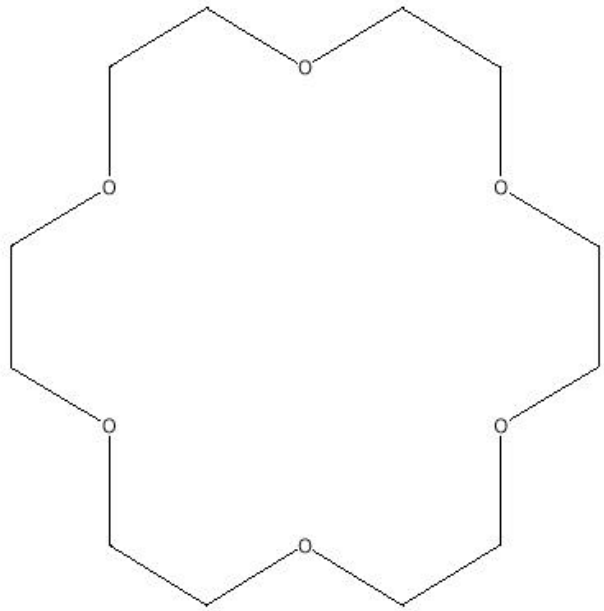
Reference: R.L.Garrell, J.C.Smyth, F.R.Fronczek, R.D.Gandour (1988) *J.Inclusion Phenom.Macrocyclic Chem.*,**6**,73

Formula: $C_{12}H_{24}O_6.2(C_2H_3N_1)$

Compound Name: 18-Crown-6 bis(acetonitrile) clathrate

Space Group:	P21/n	***Cell:***	***a***	9.123(3)	***b***	8.524(3)	***c***	13.676(4)
Space Group No.:	14	***(Å,°)***	α	90.00	β	104.68(3)	γ	90.00

R-Factor (%): 6.6 ***Temperature(K):*** 295 ***Density(g/cm^3):*** 1.118



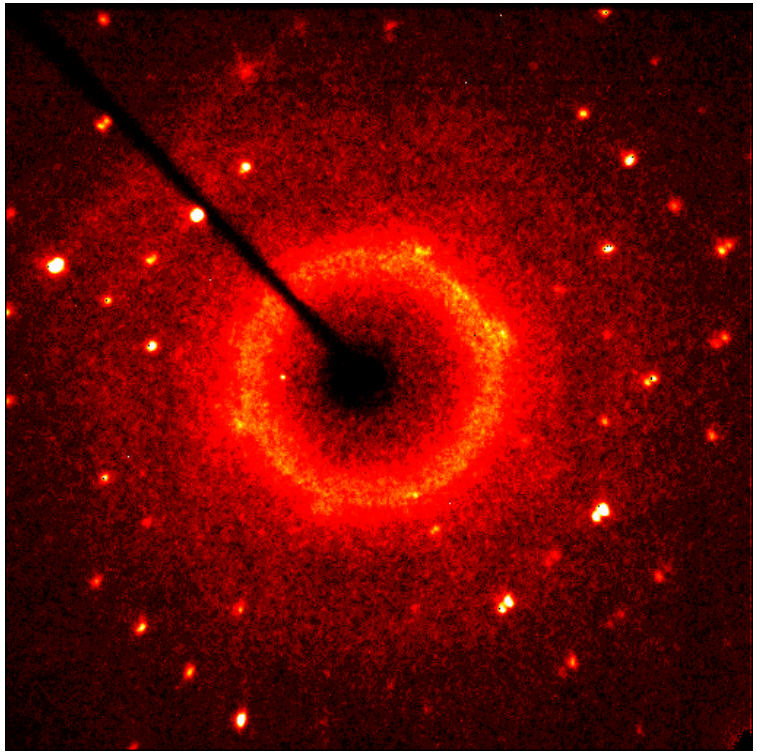
Source: Cambridge Crystallographic Data Center, Conquest 1.2

Phase Transition with onset of Non-Merohedral Twinning: An Example You Can Use in the Classroom and Lab

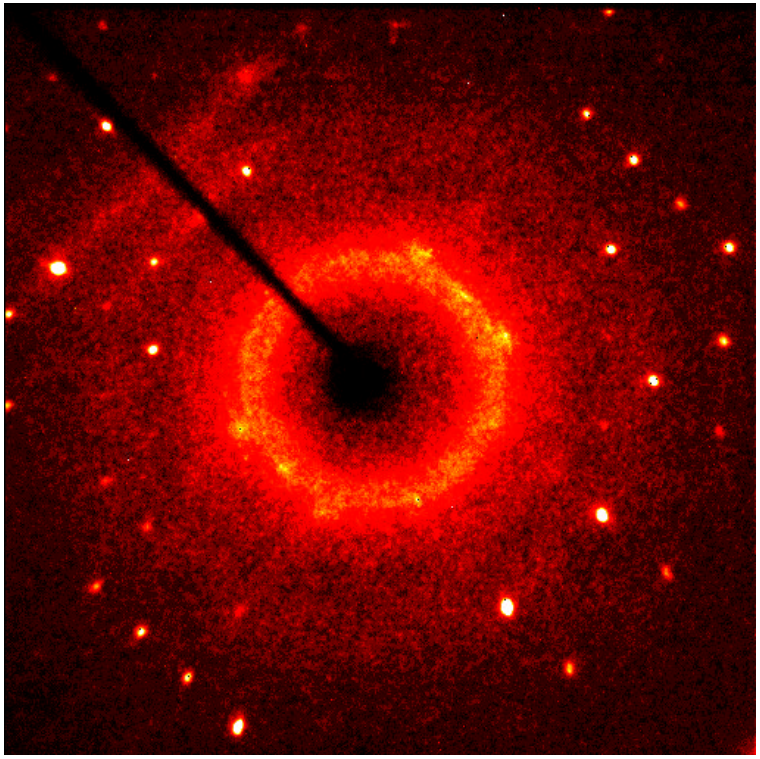
Formula	18-Crown-6 bis-(acetonitrile) clathrate	
	Phase 1(GEFREO01)	Phase 2(GEFREO)
Space group	$P2_1/n$	$P\bar{1}$
Temp, K	295	123
a, Å	9.123(3)	8.982(4)
b, Å	8.524(3)	8.343(7)
c, Å	13.676(4)	13.576(4)
a, º	90.0	91.80(8)
ß, º	104.68(3)	105.50(3)
?, º	90.0	91.28(9)
R, %	6.6	10.3

Phase 1, R.L. Garnell, J.C. Smyth, F.R. Fronczek, R.D. Gandour (1988) *J. Inclusion Phenom. Macrocyclic Chem.*, **6**, 73
Phase 2, R.D. Rogers, P.D. Richards, E.J. Voss (1988) *J. Inclusion Phenom. Macrocyclic Chem.*, **6**, 65

Phase Transition with Onset of Non-Merohedral Twinning: *hk0* Zone Image Showing the Phase Transition



163 K

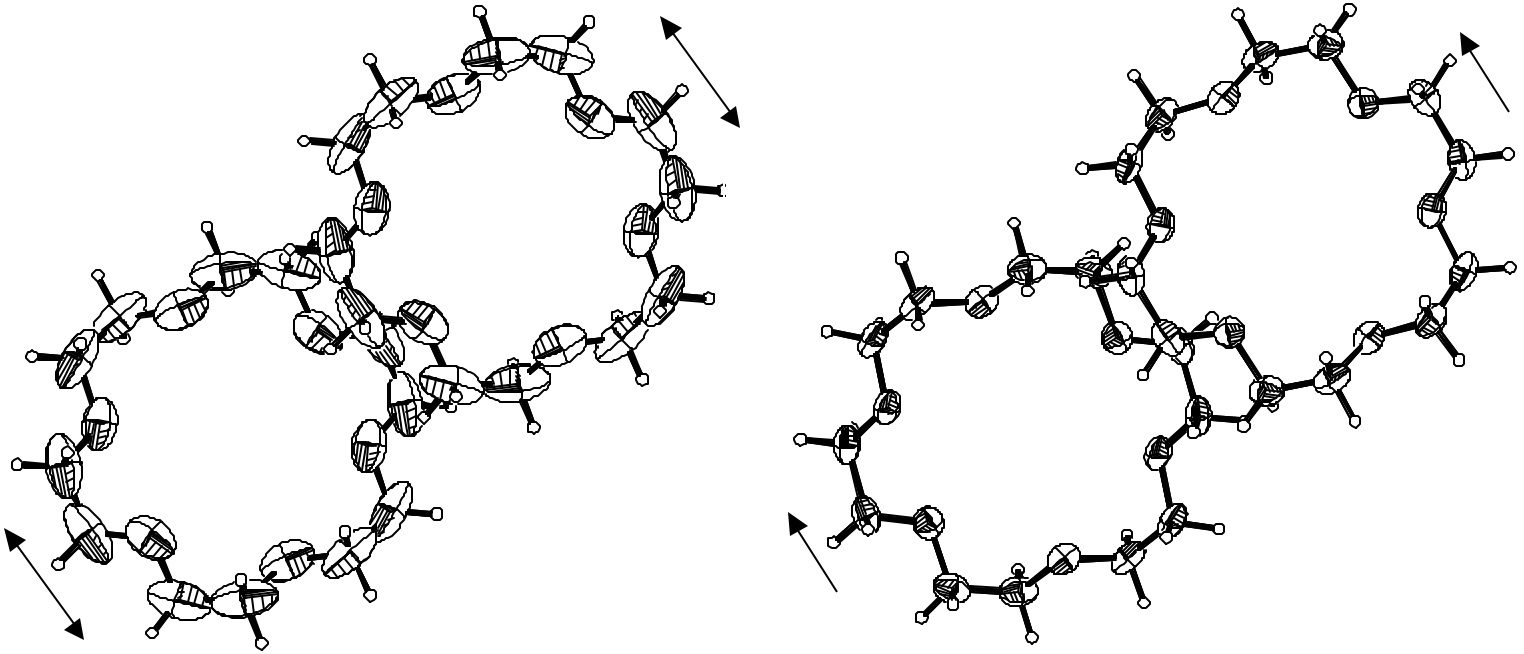


173 K

Phase Transition with Onset of Non-Merohedral Twinning: What is the Origin of the Twinning?

$P2_1/n$ at 223K – Disordered
One-half molecule unique

$P\bar{1}$ at - Ordered by "Gearing"
Two-half molecules unique



Both drawn at 50% probability, viewing (101) of monoclinic setting
The acetonitrile solvent was removed for clarity

Phase Transition with Onset of Non-Merohedral Twinning: How to Determine the Twin Law

- The **twin law** is a 3x3 matrix that allows one to convert from an *hkl* in one twin component to an *hkl* in another.
- To determine the twin law one multiples the orientation matrix of the first twin component by the second. The order is important!
- Examples 72-2/7-22 pair are exact overlaps, but 71-2/7-12 pair are partially overlapped.

A1 [Orientation matrix for primary twin component] =

0.08862 -0.06149 -0.03684
-0.04176 -0.09291 0.01899
-0.06893 -0.02897 -0.06392

unit cell parameters =

8.3561 9.0194 13.6324 105.506 91.778 91.236

A2 [Orientation matrix for secondary twin component] =

0.08860 0.06657 0.04104
-0.04168 0.09054 -0.02097
-0.06877 0.02493 0.06068

unit cell parameters =

8.3652 9.0177 13.6259 105.467 91.728 91.179

A2^{-1} * **A1** [transforms $\boldsymbol{hkl}_{\mathbf{A1}}$ to $\boldsymbol{hkl}_{\mathbf{A2}}$] = Twin Law

1.00120 0.05773 0.04734
-0.00057 -0.99981 0.00001
-0.00106 -0.00114 -0.99974

Phase Transition with Onset of Non-Merohedral Twinning: How to Determine the Rotation Axes

- The opposite operation is used to determine the rotation axes in reciprocal- and direct space.
- The Transformed **A2** * **A1**$^{-1}$ matrix is normalized.
- The rotation axes are calculated in both reciprocal- and direct space.
- The rotation angles for two-component non-merohedral twins are usually 180º.
- Twin operations are usually rotations – mirrors are very rare.

A2 * **A1**$^{-1}$ [transforms recip vec x1 to x2]=

0.09576	-0.51478	-0.85027
-0.51604	-0.75782	0.40030
-0.85127	0.40091	-0.33959

Transformed **A2** * **A1**$^{-1}$ [rotation axis along z] =

-1.00062	0.00038	-0.00007
-0.00045	-0.99987	-0.00075
0.00007	0.00075	0.99884

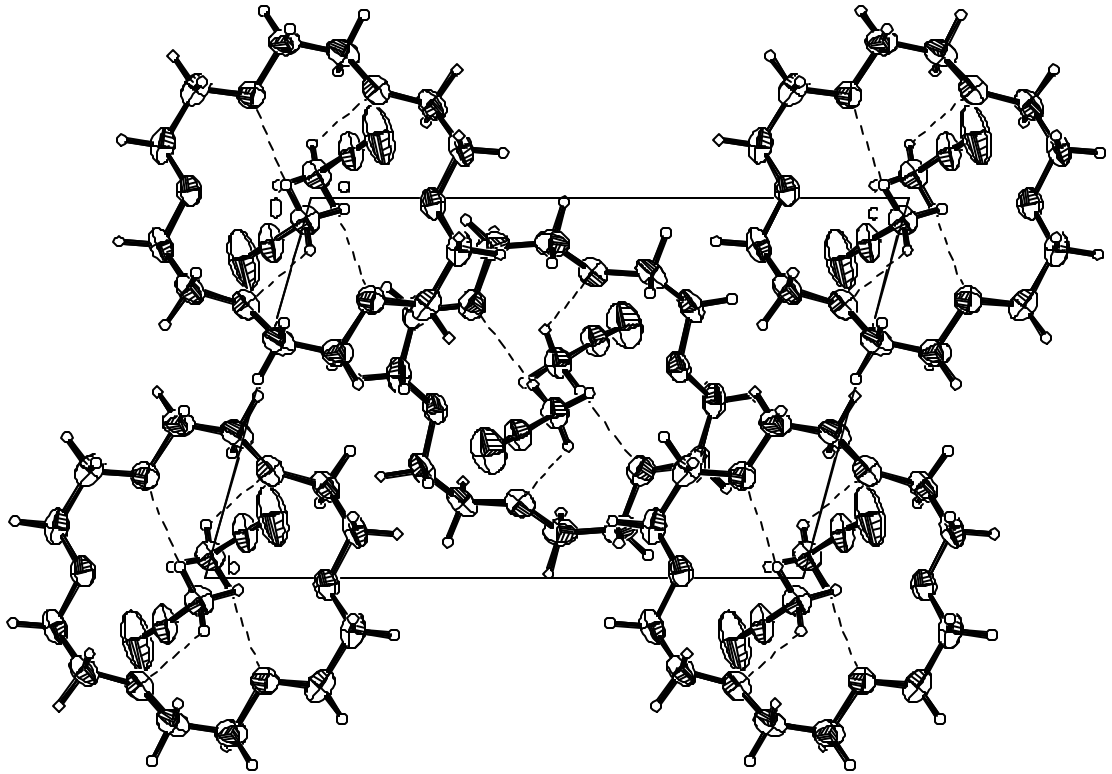
Rotation axis in reciprocal space = 1.0 0.0 0.0

Rotation around [1 0 0] = -180.0º

Rotation axis in direct space = 1.00 -0.029 -0.024

Rotation around (1.00 -0.029 -0.024) = -180.0º

How do the Twin Components fit Together?



18-Crown-6 bis-(acetonitrile) clathrate drawn with acetonitrile.
Dashed lines represent short O•••H contacts. Final R1 = 7.1%

- The twin law mandates a 180.0º rotation around (1.00 -0.029 -0.024).
- This plot views along (100).
- The 18-crown-6 rings are inclined to the view so a rotation alone will not make a clean twin interface.
- An additional shift of +(0½½) will make a clean fit, but then the unit cells of both twin components must interpenetrate at interface!

References for Several Reversible Phase Transitions Accompanied by Non-Merohedral Twinning

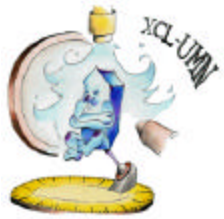
"Variable-Temperature X-Ray Structural Investigation of $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (pz = Pyrazolyl Ring): Observation of a Thermally Induced Spin State Change from all High Spin to an equal High Spin-Low Spin Mixture, Concomitant with the Onset of Nonmerohedral Twinning," D. L. Reger, C. A. Little, V. G. Young, Jr., and M. Pink, *Inorg. Chem.* **40**, 2870 (2001).

"Crystal Structures of Nitronium Tetranitratogallate and its Reversible Solid-State Phase Transition Mediated by Non-Merohedral Twinning," D. G. Colombo, V. G. Young, Jr., W. L. Gladfelter, *Inorg. Chem.* **39**, 4621 (2000).

"Making and Breaking Covalent Bonds across the Magnetic Transition in the Giant Magnetocaloric Material $Gd_5(Si_2Ge_2)$," W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A.Gschneidner, V. G. Young, Jr., and G. J. Miller, *Phys. Rev. Let.* **84**, 4617 (2000).

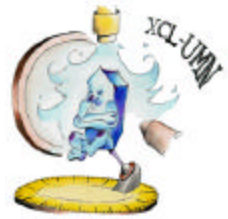
"Insulator-metal Transition in $BaCo_{0.9}Ni_{0.1}S_{2-y}Se_y$," J. W. Schweitzer, L. S. Martinson, N. C. Baenziger, D. C. Swenson, V. G. Young, Jr., I. Guzei, *Phys. Rev.* **B62,** 12792 (2000).

Non-Destructive, Reversible Phase Transitions Accompanied by Non-Merohedral Twinning



- All samples have a sharp phase transition. Some of these were monitored by other physical measurements.
- The higher temperature phase in all samples except one is found to have the higher symmetry crystal system and space group.
- The lower temperature phase always forms a non-merohedral twin in the relatively lower symmetry crystal system except for one.
- It is *truly remarkable* that in all of these examples are reversible without damage to any of the samples.
- All of the references presented here are from small molecule specimens, but it is conceivable that this phenomena could occur during the flash-freezing of protein crystals. The specimen might otherwise be mistaken to be cracked and therefore discarded.

Warning Signs for Merohedral and Pseudomerohedral Twins



- Laue symmetry does not fit for metric symmetry.
- R_{int} for a higher symmetry Laue class is slightly higher than a lower symmetry Laue class. R_{int} often is lower than that for a normal crystal.
- The reflection statistic $|E^2-1|$ value is shifted to a lower value: centrosymmetric. ~ 0.8, noncentrosymmetric ~ 0.6.
- The space group may be in either trigonal or hexagonal: 2 crystal systems with same metrics, 5 Laue classes with 15 point groups.
- The space group may be tetragonal: 2 Laue classes with 7 point groups.
- The reflection conditions are not consistent with any known space group.
- The structure cannot be solved.
- The Patterson function is physically impossible.
- The reciprocal lattice planes have a smooth variation in intensity from low to high resolution instead of a normal statistical variation.
- K-values are anomalously high.

Source: R. Herbst-Irmer and G Sheldrick, *Acta Cryst.* B**54**, 443 (1998)

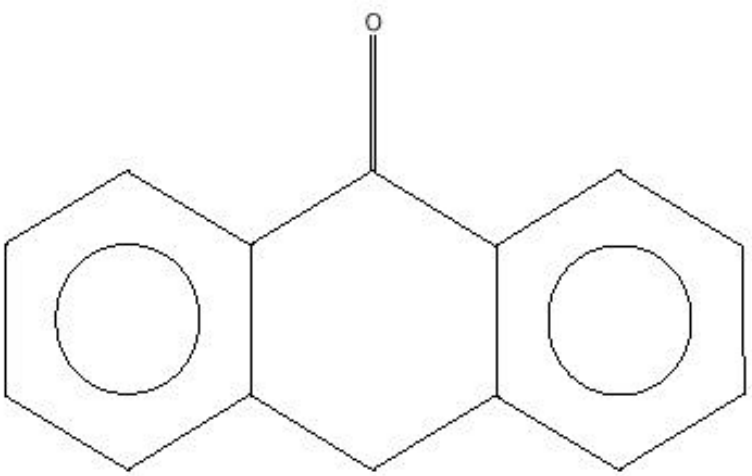
Anthrone - Is it Twinned or is it a Single Crystal?

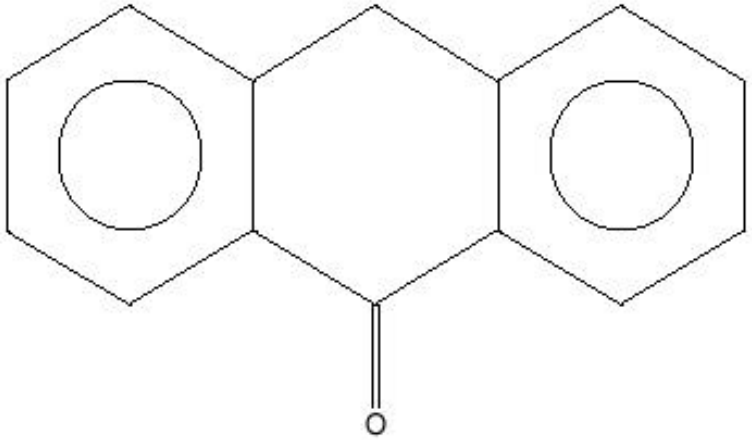
ANTRON01

Reference:	G.P.A.Yap, J.A.Wisner (1997) *Private Communication,"*						
Formula:	$C_{14}H_{10}O_1$						
Compound Name:	10-Methylene-9-anthrone						
Synonym:	Methylenanthrone						
Space Group:	P21/c	***Cell:***	***a*** 7.865(0)	***b*** 3.982(0)	***c*** 15.813(1)		
Space Group No.:	14	***(Å,°)***	α 90.00	β 101.79(0)	γ 90.00		
R-Factor (%):	4.68	***Temperature(K):***	295	***Density(g/cm³):***	1.331		

ANTRON10

Reference:	S.N.Srivastava (1972) *Indian J.Phys.*,**46**,56						
Formula:	$C_{14}H_{10}O_1$						
Compound Name:	Anthrone						
Space Group:	P21/a	***Cell:***	***a*** 15.800	***b*** 3.998	***c*** 7.860		
Space Group No.:	14	***(Å,°)***	α 90.00	β 101.67	γ 90.00		
R-Factor (%):	11.8	***Temperature(K):***	295	***Density(g/cm³):***	1.326		





Source: Cambridge Crystallographic Data Center, Conquest 1.2

Twinning in Anthrone

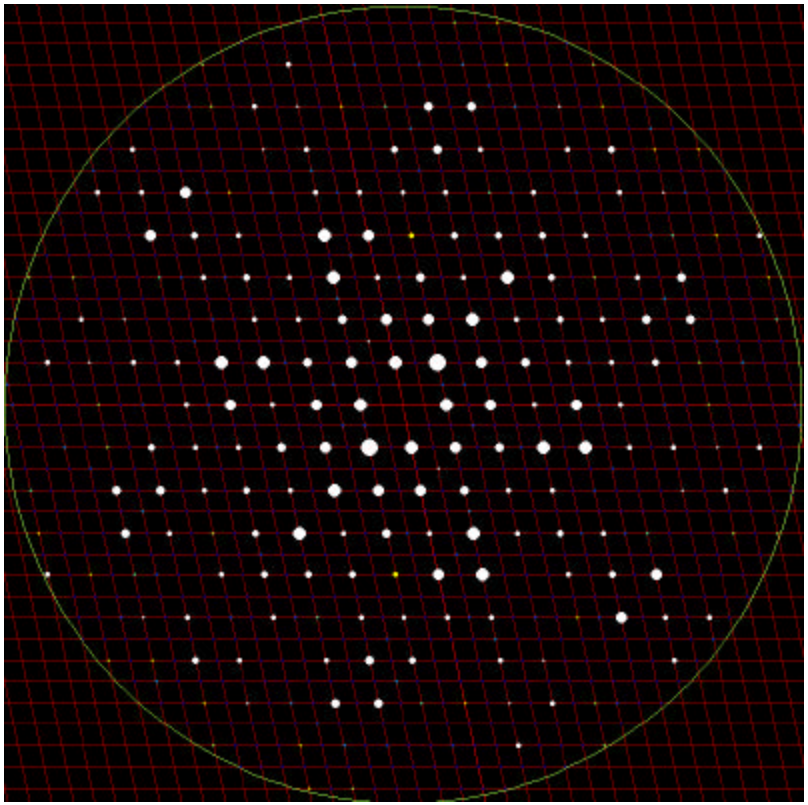
Formula	$C_{14}OH_{10}$	
CCDC entry	ANTRON10	ANTRON01
Space group	$P2_1/a$	$P2_1/c$
Temp, K	295	295
a, Å	15.800	7.865
b, Å	3.998	3.982
c, Å	7.860	15.813
a, º	90.0	90.0
ß, º	101.67	101.79
?, º	90.0	90.0
R, %	11.8	4.68

ANTRON10, S.N. Srivastava, *Indian J. Phys.*, **48**, 56 (1972).
ANTRON01, G.P.A. Yap and J.A. Wisner, Private Communcation to CCDC (1997).

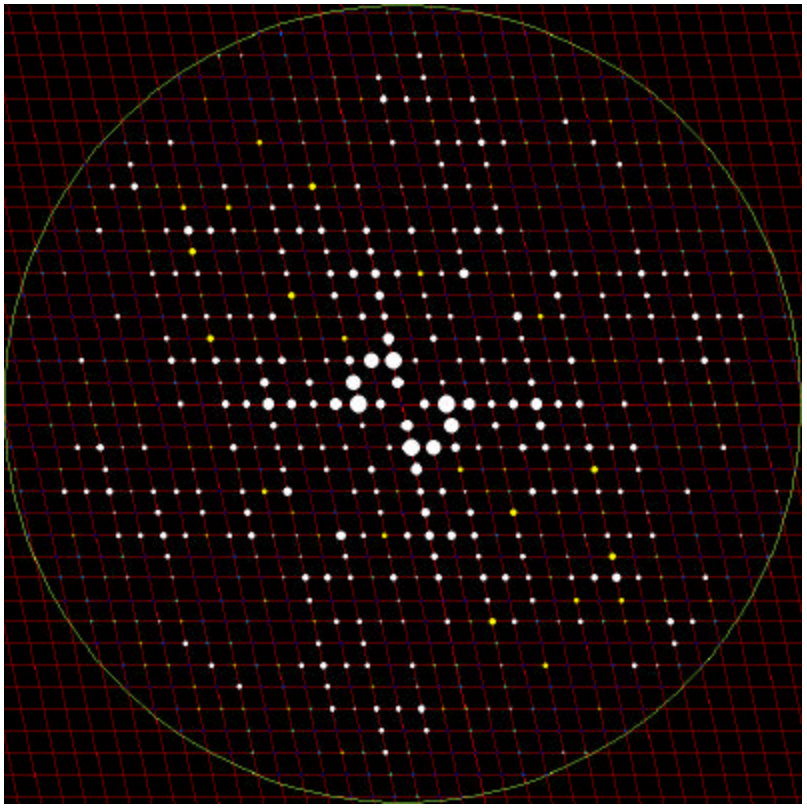
Anthrone when twinned

Both published anthrone structures have one non-unique axis about ½ of the other. The result is an apparent doubled monoclinic cell. The twinning causes additional symmetry in the reciprocal lattice.

$k = 0$



$k = 1$

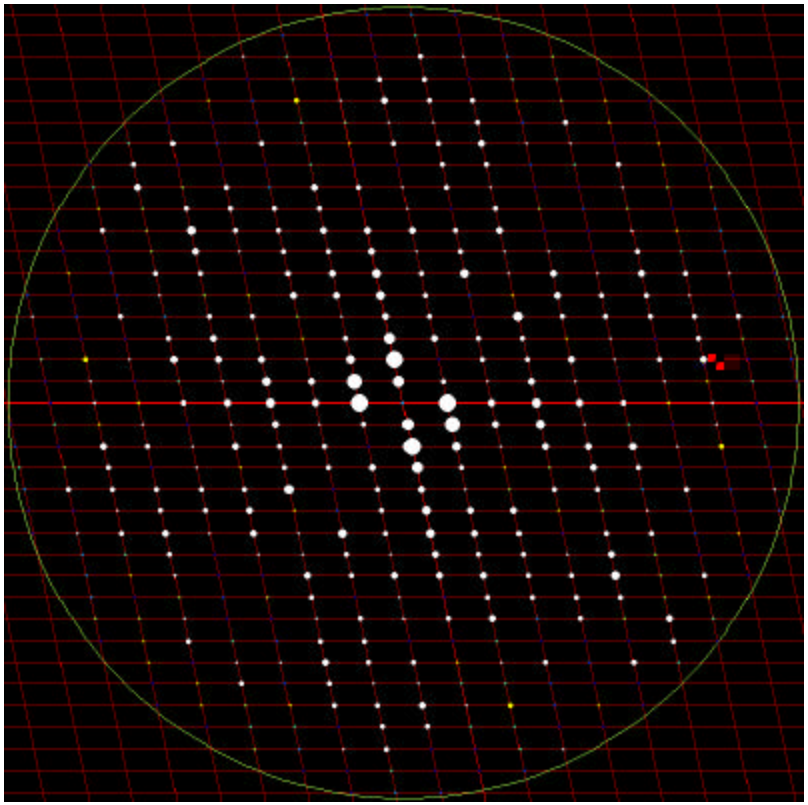


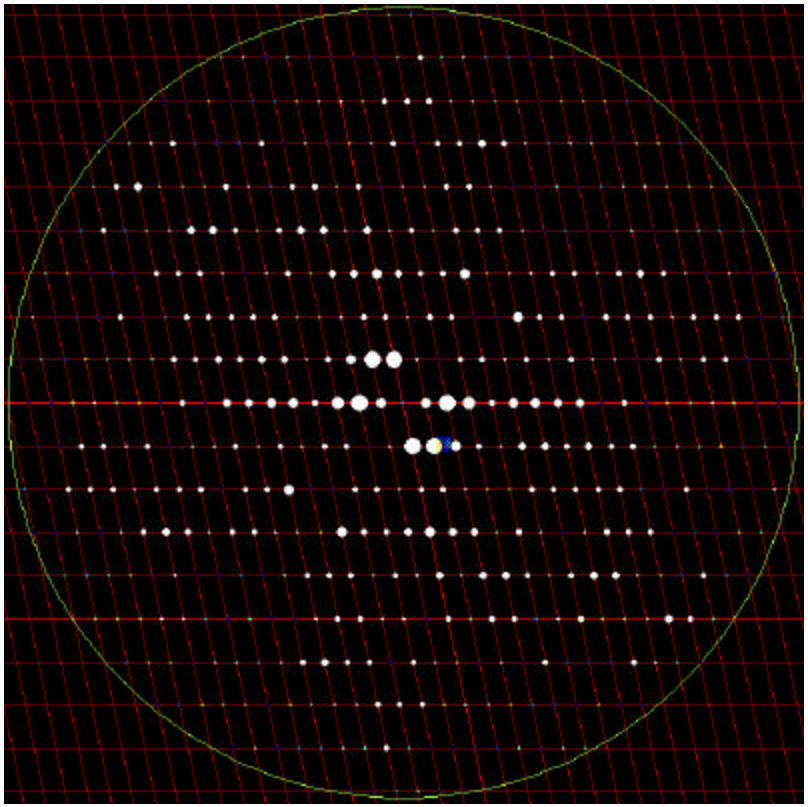
Source: L. M. Daniels, private communication

Anthrone when twinned

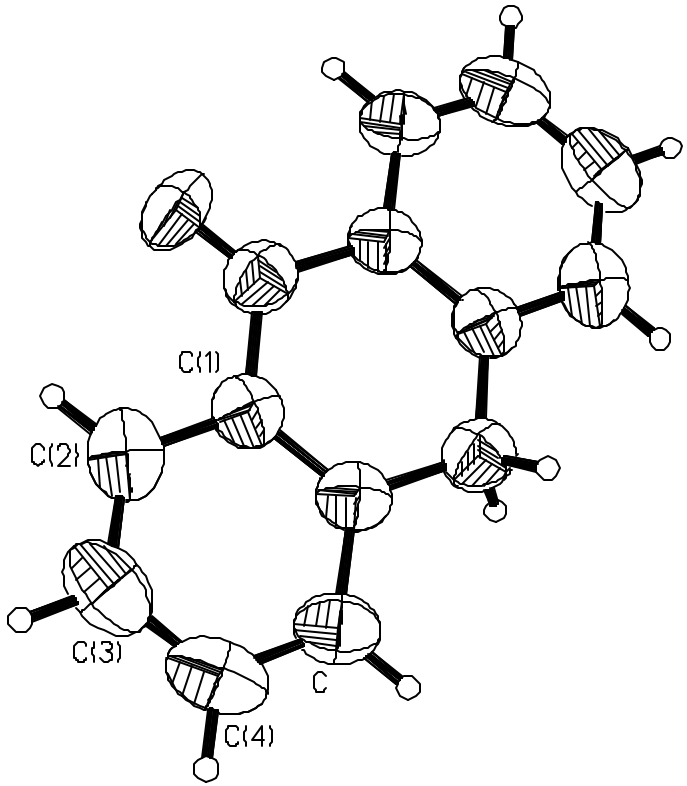
Both twin components are shown side-by-side below. *a* and *c* alternate in the two possible *hkl*: *k*=1 layers. Data must be converted to HKLF 5 format

$k = 1$





Source: L. M. Daniels, private communication


C(1)
C(2)
C(3)
C
C(4)

Acknowledgements

Neil R. Brooks

Maren Pink

Lee M. Daniels

Department of Chemistry,
University of Minnesota

Twinning *is* Beautiful

Source: Sue de Beer's *Twins*, Altoid Collections, 1998