REFINEMENT OF TWO TWINNED SINGLE CRYSTALS

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Introduction

Disorder and twinning usually cause severe problems in the course of single crystal X-ray structure determination and refinement. Especially, the existence of twinning has often prevented investigators with serial 4-circle diffractometers from successfully measuring such structures. Fact is, that twinning was once well understood by structure analysts working with Weissenberg- and precession-cameras [1]. Those scientists who are still able to work with such photographic films know that twinning is easily recognized and that reliable indexing is really problem-free with precession photographs.

The advent of serial diffractometers at the beginning of the 70's made reliable indexing and data collection more complicate. Our first Hilger & Watts (Y290), installed 1971 and still running very reliable, had no autoindexing routines in the software, which was written in PAL III assembler. The drift away from using free, open source software towards using commercial software packages without any source code, made the treatment of twins seem even more difficult.

Since the arrival of CCD- and imaging-plate-area detectors at the middle of the 90's at least the non-merohedral twinning is a much better recognized and understood problem [2]. Especially, CCD detectors can easily find the centers of many reflections in a very short period of time. If the normal single crystal indexing programs fail, special programs for the visualization of all reflections exist and the determining of reflection indices, cell parameters and orientation matrices for all components for the twinned crystal should be no problem [3].

We now present two twinned structures with $Z' = 3$ and a three-fold primitive unit-cell. The first example represents an organic structure, while the other is from organometallic chemistry. We will describe how the twinning was recognized, measured and solved and how the twin matrix was derived. Different refinement strategies with the SHELXL97 [4] program will also be discussed.

Example 1

Compound `wro`, $C_{22}H_{34}N_2O_6$, is an isomer of compound `ntb` [5]. Initial rotation photos showed that, at least, one axis must have an axial length of over **45** Å. Therefore, one crystal of compound `wro` was mounted on a Nonius CAD4 with Cu $K\alpha$ radiation. All reflections from an input list of 16 reflections could be indexed without any problems. The following cell parameters were found and refined from 25 reflections (within a θ-range from: $42.7° \rightarrow 46.5°$): $a = 11.979(1)$, $b = 12.065(1)$, $c = 48.988(5)$ Å, $\alpha = \beta = \gamma = 90.0°$.

A Laue check gave only $2/m$ symmetry instead of the expected mmm symmetry for an orthorhombic lattice. Therefore, the data collection was done with the following hkl index range: h: $0 \rightarrow 15$; k: $-15 \rightarrow 0$, l: $-61 \rightarrow 61$. A dataset of 16454 reflections was measured.

The Bruker $SHELXTL - Plus$ program $XPREP$ [6] gave a $R_{int} = 0.521$ for orthorhombic higher METRIC symmetry (as expected from the above mentioned Laue check). Furthermore, $XPREP$ could not find any acceptable space group, even after changing the tolerances. In the monoclinic case the R_{int} value is 0.023 and the space group is $P2_1/a$ (No. 14).

Prgogram XS [6] gave a clear solution with 3 independent molecules with 30 non-H atoms in the asymmetric unit each. This solution showed the expected molecule, but a refinement with program XL [6] stopped at a R-factor of 0.3. It was not possible (with all known tricks) to refine the solution to a smaller R-factor.

There were some typical warning signs of twinning: **1.** Of 16454 measured reflections only 6594 are significant. **2.** The mean value of $|E^2 - 1|$ was with 1.341 very high (expected value: 0.968). A critical look in the reciprocal space with the new developed program $PRECESSION$ [7] very quickly showed strange systematic absences, as shown in the screenshot of the h-2l layer (Fig. 1).

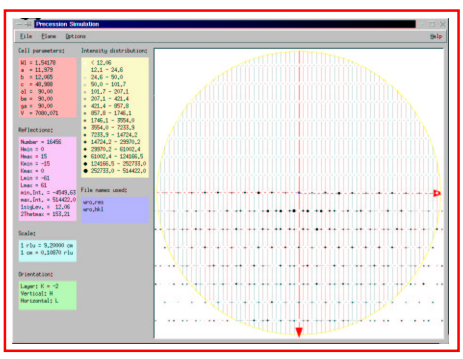

Fig. 1: Screenshot of program $PRECESSION$ [7]. The strange systematic absences of the h-2l layer of compound `wro` are clearly seen. This programm is menu-driven and easy to use.

Tab. 1: Crystallographic data of compound `wro`.

molecular formula	$C_{22}H_{34}N_2O_6$
molecular mass	$M = 422.51$
crystal system	monoclinic
space group	$P2_1/a$ (No. 14)
cell parameter	$a = 11.979(1)$ Å
	$b = 12.065(1)$ Å
	$c = 48.988(5)$ Å
unit-cell volume	$V = 7080.1(11)$ Å^3
number of molecules	$Z = 12$
calculated density	$\rho_c = 1.189$ g·cm^3
crystal size	$0.7 \times 0.6 \times 0.2$ mm
linear absorption coefficient	$\mu = 0.707$ mm^{-1}
2θ-range	$4.8° \rightarrow 153.1°$
wavelength [Cu $K\alpha$]	$\lambda = 1.54178$ Å
measured reflections	16456
symmetry independent reflections	8935
significant reflections	6333 $[F^2 > 2\sigma(F^2)]$
number of parameters	317
goodness of fit	$S = 1.008$
R-factors	$R = 0.0603$
diffractometer	Nonius CAD4

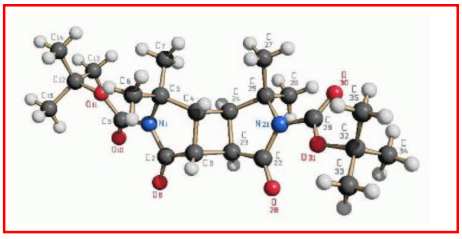

Fig. 2: Molecular structure of compound `wro`.

Tab. 2: $SHELXL97$ [4] file `wro.ins` of compound `wro`.

```
TITL C22 H34 N2 O6                                        WRO twin
CELL 1.54178  11.979  12.065  48.988  90.00  90.00  90.00
ZERR  12.00   0.001   0.001   0.005   0.00   0.00   0.00
LATT 1
SYMM .5-X, .5+Y, -Z
SYMM .33333+X, Y, .33333+Z
SYMM .66667+X, Y, .66667+Z
SYMM .16667-X, .5+Y, .66667-Z
SYMM .83333-X, .5+Y, .33333-Z
SFAC C H N O
UNIT 264 408 24 72
TWIN 1 0 0  0 -1 0  0 0 -1
ACTA
TEMP 20
SIZE 0.7 0.6 0.2
L.S. 4
BOND $h
CONF
FMAP 2
PLAN -5
WGHT    0.1165      5.7485
EXTI    0.002114
BASF    0.13574
FVAR    1.66880
N1    3    0.60153    0.39951    0.66899    11.00000    0.04363    0.04488 =
         0.03819   -0.00017   -0.00084    0.00647
C2    1    0.57523    0.41104    0.64709    11.00000    0.04262    0.05426 =
         0.04235   -0.00340   -0.00118    0.00281
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
AFIX 137
H351    2    0.11070    0.57743    0.51633    11.00000    0.16089
H352    2    0.14691    0.68071    0.49905    11.00000    0.12698
H353    2    0.16414    0.68054    0.53077    11.00000    0.18470
HKLF 4
REM  C22 H34 N2 O6                                        WRO in P2(1)/a
REM R1 =  0.0659 for   6333 Fo > 4sig(Fo)  and  0.0865 for all   8265 data
REM       317 parameters refined using      0 restraints
END
```

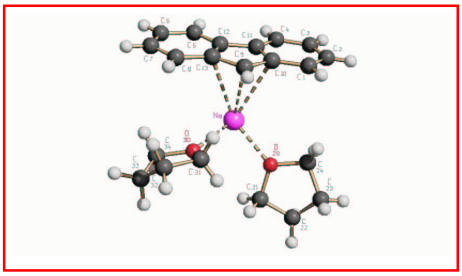

Fig. 3: Molecular structure of compound `nafl`.

Example 1 (continued)

There are strong reflections in every third plane $\pm 3nkl$ perpendicular to **a** and in every third plane $hk \pm 3n$ perpendicular to **c** and much weaker reflections in the reciprocal layers between. This is the reason for the anomalously high value for the mean of $|E^2 - 1|$. The interpretation is very easy (see also the `printout` of layer h-2l):

The common (metrically) orthorhombic super-lattice can be constructed from the monoclinic sub-lattice of the overlapped reflections. The single individuals belong to space group $P2_1/a$ with the following cell parameters: $a = 11.979(1)$, $b = 12.065(1)$, $c = 16.810(2)$ Å, $\beta = 103.74(1)°$, $V = 2360.0(4)$ Å^3 and form a three-fold primitiv unit cell $(0, 0, 0; 1/3, 0, 1/3; 2/3, 0, 2/3)$.

The twin law is especially easy in the orthogonal unit cell:
$2 \parallel$ **a**: $\mathbf{R} = (100, 0\bar{1}0, 00\bar{1})$ or
$m \perp$ **a**: $\mathbf{R} = (\bar{1}00, 010, 001)$.

In Table 2 the first twin law is applied.

Example 2

Compound `nafl`, $[Na(C_{13}H_9)(C_4H_8O)_2]_n$, was prepared by Dr. Falk Olbrich, University of Magdeburg, Germany. One yellow crystal was transferred directly on a SMART 1000 System with low-temperature device, because this compound is very air- and moisture-sensitive. Auto-Indexing gave a very large cell with one axis over **50** Å and a smaller cell with the following cell parameters: $a = 9.638(2)$, $b = 10.120(2)$, $c = 19.170(3)$ Å, $\beta = 99.65(1)°$, $V = 1843.4(5)$ Å^3. The data collection was done with this orientation matrix, program XS [6] gave again a clear solution, but the refinement with XL [6] stopped at 35%.

Therefore, another crystal of compound `nafl` was mounted on a Nonius CAD4 with Cu $K\alpha$ radiation. An orthorhombic cell with mmm symmetry was found and measured: $a = 9.638(2)$, $b = 10.120(2)$, $c = 56.698(11)$ Å, $V = 5530.1(19)$ Å^3. Program $PRECESSION$ showed the same strange systematic absences as compound `wro`. Therefore, the refinement with $SHELXL97$ was done with the same twin matrix and gave a final R-factor of 0.071.

Results

The two solved structures belong to twin class IV [8]. In this class some reflections completely overlap and some behave as single crystal data. This kind of twinning is sometimes also characterized as **partial merohedral twinning.**

The common orthorhombic super-lattice of the twin individuals can be constructed from the monoclinic sub-lattice of the overlapped reflections. In our cases the single individuals belong to space group $P2_1/a$ and form a three-fold primitive (0,0,0; 1/3,0,1/3; 2/3,0,2/3) unit cell.

References

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