SOLUTION AND REFINEMENT OF A MEROHEDRALLY TWINNED SINGLE CRYSTAL

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Introduction

Merohedral twinning is a frequently observed and often undetected complication in single crystal X-ray crystallography. It usually causes severe problems in both structure determination and refinement [1, 2]. Especially, on diffractometers with CCD- or Imaging-Plate-Detectors twinning by merohedry is difficult to realize, because these twins have domains with diffraction patterns that are completely overlapped [3, 4]. Fortunately, this kind of twinning is only possible in trigonal, hexagonal, tetragonal and cubic crystal systems.

Ten years ago we solved and refined the merohedrally twinned structure of L-threitol [5]. At that time this was a difficult task, because only serial diffractometers were available and the only program for refining such a structure was a specially adapted version of the old ORXFLS program of Busing and Levy [6]. It was also possible to refine the structure of L-threitol with a beta-test version of SHELXL-92 [5].

We now present the merohedrally twinned structure of 2-(Diphenylphosphinoyl)-2-phenylethenol, $C_{20}H_{17}O_2P$. We will describe how the twinning was recognized and how the twin matrix was derived. Different refinement strategies with the SHELXL-97 [7] program will also be discussed.

Tab. 1: Crystallographic data of compound `dmso`

Crystal data	
$C_{20}H_{17}O_2P$	Mo $K\alpha$
$M_r = 320.31$	$\lambda = 0.71073$ Å
trigonal	Cell parameters from 9999 reflections
$P3_1$ (No. 144)	$\theta = 2.4 - 32.5°$
$a = 19.755(1)$ Å	$\mu = 0.707$ mm^{-1}
$c = 11.236(1)$ Å	$T = 293(2)$ K
$V = 3797.5(4)$ Å^3	blocks
$Z = 9$	$0.5 \times 0.4 \times 0.4$ mm
$D_x = 1.261$ g·cm^3	Colorless
D_m not measured	
Data collection	
Bruker APEX CCD diffractometer	$R_{int} = 0.0672$
ϕ and ω scans	$\theta = 32.5°$
Absorption correction: multi-scan	$h = -29 \rightarrow 29$
102635 measured reflections	$k = -29 \rightarrow 29$
18233 independent reflections	$l = -16 \rightarrow 16$
15600 significant reflections	no standard reflections
$I > 2\sigma(I)$	intensity decay: 0%
Refinement	
Refinement on F^2	$(\Delta/\rho)_{max} = 2.256$
$R[F^2 > 2\sigma(F^2)] = 0.0389$	$\Delta\rho_{max} = 0.347$ e Å^{-3}
$wR(F^2) = 0.0829$	$\Delta\rho_{min} = -0.283$ e Å^{-3}
$S = 0.965$	Extinction correction: *SHELXL*
18233 reflections	Extinction coefficient: 0.0000(2)
678 parameters	
H atoms treated by a mixture of independent and constrained refinement	Scattering factors from *International Tables for Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$	Absolute structure: Flack (1983)
	Flack parameter = −0.07(4)

Experimental

Compound `dmso`, $C_{20}H_{17}O_2P$, was pepared by Jordanka Petrova et al. [8]. Very nice, colorless crystals were grown from DMSO (Dimethyl-sulfoxid).

From rotation- and Weissenberg-photographs of different crystals of `dmso`, the Laue class $\bar{3}12/m$ was determined. The intensity measurement was done on a Hilger & Watts (Y290) diffractometer eight years ago. 6375 reflections were measured. In connection with the observed extinction conditions $l = 3n$ for $00l$ reflections, the only space groups are: $P3_112$ and $P3_212$. All attempts to solve the structure by direct methods and Patterson-method did not succeed. Therefore, the lower symmetric space groups $P3_1$ and/or $P3_2$ were tried. After some trials, the program SHELXS-86 [9] succeeded in solving the structure in space group $P3_2$. All atoms of the three crystallographically independent molecules were found in successive difference maps. This solution showed the expected molecular geometry of the molecules, but the refinement with program SHELXL-93 stopped at a R-value of 25%. It was not possible to refine the solution to a smaller R-factor.

There were some typical warning signs for twinning: **1.)** The mean value of $|E^2 - 1|$ was 0.557 (expected value: 0.736). **2.)** All F_o^2 values are consistently larger than the corresponding F_c^2 values.

The structure could not be refined successfully until the twin matrix in **Table 2** was found. This matrix was derived from the Table: "Merohedral Twins in the Trigonal/Hexagonal Crystal System" [2]. It represents a mirror in the crystal. In enantiomorphic space groups it is neccessary to determine the correct space group. Since inversion twinning is also possible **four** possibilities have to be tested (see **Table 3**).

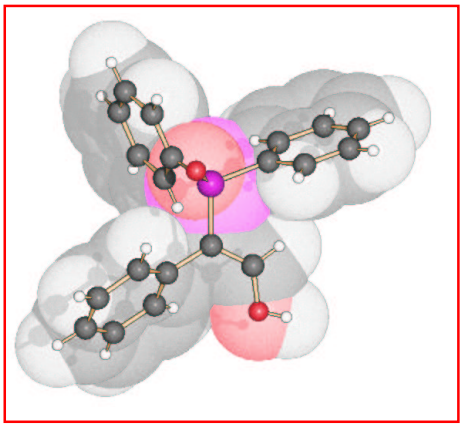

Fig. 1: Molecular structure of compound `dmso`

Tab. 2: *SHELXL-97* [7] input-file: `dmso.ins`

```
TITL 3 * (C20 H17 O2 P)                          DMSO in P3(1)
CELL 0.71073  19.755  19.755  11.236  90.00  90.00 120.00
ZERR    9.00   0.001   0.001   0.001   0.00   0.00   0.00
LATT -1
SYMM -Y, X-Y, .33333+Z
SYMM -X+Y, -X, .66667+Z
SFAC C H O P
UNIT 180 153 18 9

ACTA
SIZE 0.5 0.4 0.4
TEMP 20

TWIN   0 -1 0    -1 0 0    0 0 -1        <-- This is the correct twin matrix

L.S. 4
BOND $h
CONF
HTAB
FMAP 2
PLAN -10

WGHT    0.049300
EXTI    0.000000
BASF   0.50372
FVAR       0.21987
MOLE   1
P1    4   -0.095418    0.071837    1.000435    11.00000    0.03632    0.03481 =
           0.03022    0.00184    0.00283    0.02128
O11   3   -0.158826   -0.012624    1.009595    11.00000    0.04518    0.03891 =
           0.04776    0.00735    0.00242    0.01963
O12   3    0.016457    0.156171    0.696823    11.00000    0.04792    0.06269 =
           0.03701    0.01443    0.01174    0.03392
AFIX 147
H12   2    0.061238    0.165310    0.685245    11.00000    0.04443
AFIX   0
C111  1   -0.121367    0.132763    1.084988    11.00000    0.04509    0.05089 =
           0.03992   -0.00873   -0.00142    0.03163
C112  1   -0.164157    0.103963    1.188552    11.00000    0.05668    0.06547 =
           0.05875   -0.01045    0.01679    0.02359
AFIX 43
H112  2   -0.183312    0.052150    1.210594    11.00000    0.04223
AFIX   0
C113  1   -0.178354    0.153775    1.260006    11.00000    0.05877    0.10651 =
           0.07448   -0.03293    0.02260    0.02957
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C337  1    1.191506    0.545602    0.097553    11.00000    0.03781    0.02960 =
           0.03165   -0.00061   -0.00098    0.01501
AFIX 43
H337  2    1.199260    0.585006    0.150560    11.00000    0.02904
HKLF 4   1   -1 0 0   0 -1 0   0 0 1
REM  3 * (C20 H17 O2 P)                          DMSO in P3(1)
REM R1 =  0.0389 for  15600 Fo > 4sig(Fo)  and  0.0459 for all  18233 data
REM    678 parameters refined using      1 restraints
END
```

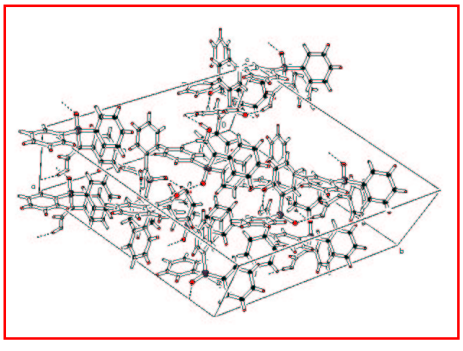

Fig. 2: Unit cell with hydrogen bonds of compound `dmso`

Tab. 3: Finding the correct space group for compound `dmso`

Space group	Twin matrix	R1	wR2	K2	Flack x
$P3_1$	mirror	0.0391	0.0835	0.5036	0.48(4)
$P3_1$	mirror + inversion	0.0389	0.0829	0.5037	-0.07(4)*
$P3_2$	mirror	0.0391	0.0836	0.5038	0.51(4)
$P3_2$	mirror + inversion	0.0393	0.0842	0.5037	1.06(4)

Tab. 4: Hydrogen-bonding geometry (Å, °) for compound `dmso`

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···O11	0.819	1.750	2.548(3)	164.19
O22—H22···O21	0.820	1.801	2.585(3)	159.65
O32—H32···O31	0.821	1.758	2.570(2)	169.14

Results

Compound `dmso`, $C_{20}H_{17}O_2P$, crystallizes in the space-group $P3_1$ ($R_{int} = 0.039$) pretending to be $P3_112$ ($R_{int} = 0.041$) as a result of merohedral twinning with nine molecules (Z' = 3) in the unit cell of a = 19.755(1) and c = 11.236(1) Å. Merohedrally twinned crystals of compound `dmso` were measured on a Hilger & Watts (Y290) and later on a Bruker APEX CCD diffractometer. After some difficulties in solving the structure, all atoms of the three crystallographically independent molecules were located in successive difference maps. Starting from this model, the refinement was performed against the original twinned data set using the program SHELXL-97 [7]. Unlike L-threitol [5] compound `dmso` does not possess a twofold axis symmetry. The final crystallographic R-value is 4.6% for all reflections.

Each molecule of the asymmetric unit contains a hydroxl group. Therefore, all molecules are held together by a system of strong hydrogen bonds, which consist of infinite chains in the direction of the shorter c axis (see **Table 4**). All oxygen atoms are involved as donors and acceptors. The hydrogen bonding scheme is shown in **Fig. 2**.

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