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Twinning by merohedry in cyclohexanone oxime: a revised structure

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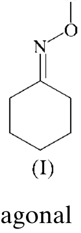
The crystal structure of cyclohexanone oxime, $C_6H_{11}NO$, was reported as severely disordered in the trigonal non-centrosymmetric space group *P*3 [Olivato, Ribeiro, Zukerman-Schpector & Bombieri (2001). *Acta Cryst.* B**57**, 705–713]. Reinvestigation of the crystal structure as twinned by merohedry in the trigonal centrosymmetric space group $P\overline{3}$, with a twofold rotation about [001] as twin law, resulted in a well ordered structure and low *R* values. The asymmetric unit contains three independent molecules, existing as a hydrogen-bonded trimer, having an $R_3^3(9)$ graph set.

Comment

The oxime moiety can both donate and accept hydrogen bonds, which makes it a very interesting building block in supramolecular chemistry (Bertolasi *et al.*, 1982; Chertanova *et al.*, 1994). Most oximes crystallize as dimers (*e.g.* DL-carvoxime; Oonk & Kroon, 1976), but there are also cases of trimeric (*e.g.* acetoxime; Bierlein & Lingafelter, 1951), tetrameric [*e.g.* (*E*)-benzaldehyde oxime; Jerslev, 1983] and polymeric (*e.g.* 2*H*-benzocyclobuten-1-one oxime; Viossat *et al.*, 1986) motifs. One of the trimeric examples is cyclohexanone oxime, (I). The reported crystal structure was refined with a disorder model and final disagreement factors were unexpectedly high (Olivato *et al.*, 2001). As part of our studies of oximes in the solid state (Marsman *et al.*, 2000), we decided to re-examine this crystal structure using a new data collection.



(I)

Our unit cell has a hexagonal metric, which is consistent with the literature data. A first inspection of the diffraction data shows that for the Laue groups $\overline{3}$ and 6/*m*, the merging *R* values (0.0514 and 0.0542, respectively) are very similar. We interpret this similarity as a strong indication of twinning. Because all reflections in the diffraction images have been indexed and no splitting of reflections is observed, the twinning must be (pseudo)merohedral.

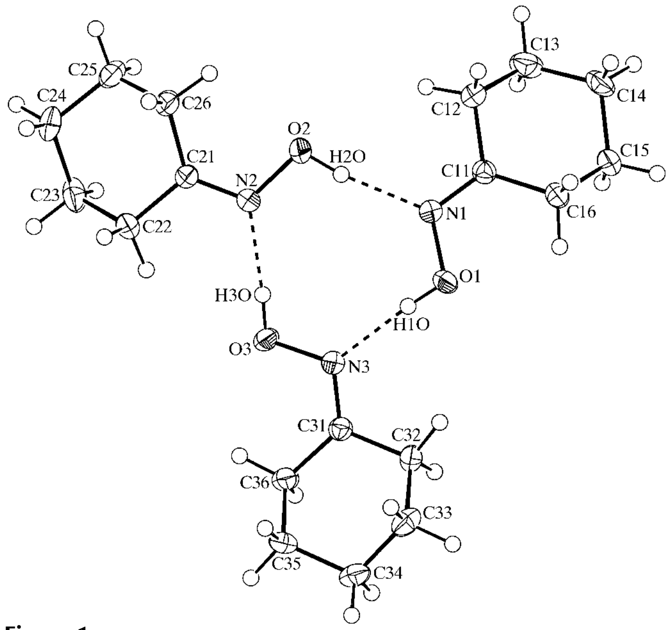


Figure 1
The three independent residues of (I), linked by hydrogen bonds into a trimeric structure. Displacement ellipsoids are shown at the 50% probability level.

Systematic space-group extinctions are not present. In contrast to the previously determined structure, which was reported in space group *P*3, the present structure was solved in the centrosymmetric space group $P\overline{3}$. However, the refinement converges at high *R* values, with residual density in the difference Fourier map. A coset decomposition (Flack, 1987) of point group 6/*m* with respect to $\overline{3}$ gives

$$\{E; 3; 3^2; i; \overline{3}; \overline{3}^5\} + \{6; 2; 6^5; \overline{6}; m; \overline{6}^5\}.$$

Any element of the second coset might be the twin operation. It transpires that the twofold rotation about [001] or, correspondingly, the mirror perpendicular to [001] are the correct merohedral twin operations (see also Giacovazzo, 2002). This result can also be obtained using the program *ROTAX* (Cooper *et al.*, 2002) or the *TWINROTMAT* routine of *PLATON* (Spek, 2003). Both programs use the difference between observed and calculated structure factors, *i.e.* $I_{obs} >> I_{calc}$, to suggest the twin law. After implementing the twin law in the *SHELXL*97 refinement (Herbst-Irmer & Sheldrick, 1998), good *R* values and a clean residual-density map are achieved. The value of the twin fraction refined to 0.5295 (14).

As a further proof for the reported revision, we refined our model and twin law against the structure factors deposited by Olivato *et al.* (2001). This refinement, (II), leads to essentially the same result, *i.e.* no disorder, low *R* values, a clean residual-density map and a twin fraction of 0.4515 (13). The minor differences, namely a 0.3% smaller unit-cell volume and

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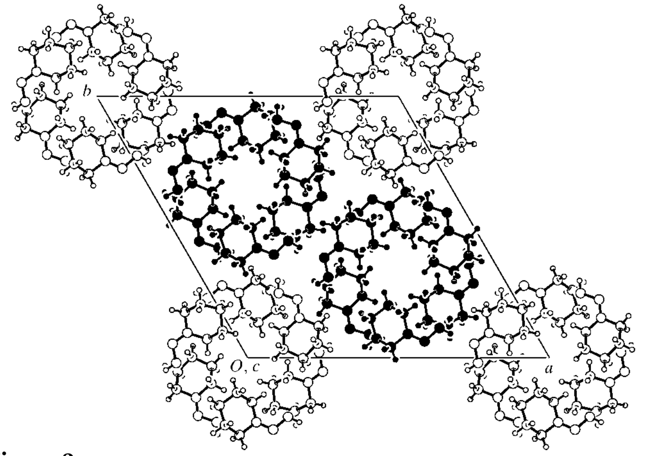

Figure 2
A view along the c axis. Residues 1 and 2 are solid, while residue 3 is unfilled.

slightly smaller displacement parameters, can be explained by the use of different crystals and different measurement temperatures (100 *versus* 110 K).

The asymmetric unit consists of three independent molecules of (I), with very similar bond lengths and angles (Table 1). The six-membered rings are in a chair conformation, which is slightly distorted because of the presence of the double bond of the oxime group. The N—O bond is eclipsed with the C1—C6 bond of the six-membered ring, with torsion angles of 1.8 (2), 1.3 (2) and −2.8 (2)°, respectively.

The three independent molecules are linked by intermolecular hydrogen bonds into a trimeric structure (Fig. 1 and Table 2). Thereby, the oxime O atoms act as hydrogen-bond donors and the N atoms as acceptors, thus generating an $R_3^3(9)$ graph set (Bernstein *et al.*, 1995). The oxime groups have an *anti* conformation, with C—N—O—H torsion angles of −169.5 (11), 176.8 (10) and 172.3 (15)°, respectively. The trimer has no crystallographic symmetry, because two of the molecules have the same chair conformation (residues 1 and 2), while one molecule has an inverted-chair conformation (residue 3). These inverted conformations are best described by a ring-puckering analysis (Cremer & Pople, 1975); residues 1 and 2 have θ values of 170.9 (2) and 171.06 (19)°, and φ values of 352.2 (13) and 349.6 (13)°, respectively. The inverted conformation of residue 3 results in a θ value of 9.30 (19)° and a φ value of 180.4 (12)°.

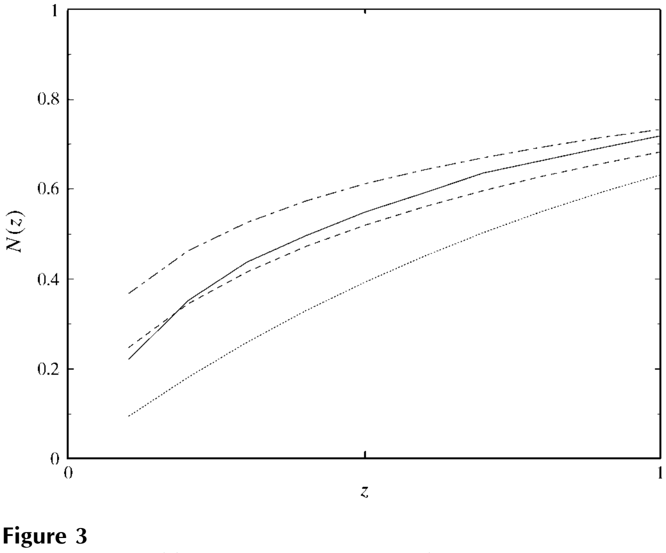

Figure 3
A cumulative $N(z)$ probability distribution (observed data: solid line; acentric: dotted line; centric: dashed line; hypercentric: dot–dashed line).

The cyclohexane rings of residues 1 and 2 are arranged about the threefold axis at $\frac{1}{3}$, $\frac{2}{3}$, z. The cyclohexane rings of residue 3 are located about the $\overline{3}$ site at 0, 0, 0 (Fig. 2). There are small solvent-accessible channels in the z direction, which amount to 2 × 25 Å^3 per unit cell at the threefold axes and to 18 Å^3 per unit cell at $\overline{3}$. In total, 2.3% of the unit cell is void, leading to a packing index (Kitajgorodskij, 1973) of only 67.3% and a low density of 1.160 Mg m^{-3}. These channels might also explain the diffuse scattering reported by Olivato *et al.* (2001) and the slightly enlarged displacement ellipsoids of the present structure.

Averaging of the 3 and $\overline{3}$ sites leads to a hexagonal subcell with a volume of $\frac{1}{3}$ and an a axis of 12.115 Å. This subcell has been reported by Olivato *et al.* (2001) and Okaya *et al.* (1956). Indeed, we find this pseudo-translational symmetry in a hypercentric behaviour of the cumulative $N(z)$ probability distribution of the observed twinned data (Fig. 3); $\langle E^2 - 1\rangle$ is 0.982. Based on calculated untwinned structure factors, the average intensity of reflections hkl ($h + 2k = 3n$) is 30 464.5, and for all other reflections it is 6798.4.

Experimental

Suitable single crystals of (I) were grown by sublimation of the commercially obtained material (Fluka Chemie GmbH) at a temperature of 333 K and a pressure of 0.97 mbar (1 mbar = 100 Pa). The preparation of the crystals used for refinement (II) is described by Olivato *et al.* (2001).

Refinement (I)

Crystal data

$C_6H_{11}NO$
$M_r = 113.16$
Trigonal, $P\overline{3}$
$a = 20.9830$ (2) Å
$c = 7.6436$ (1) Å
$V = 2914.50$ (5) Å^3
$Z = 18$
$D_x = 1.160$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 61 960 reflections
$\theta = 1.9$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 110$ (2) K
Block, colourless
0.30 × 0.21 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
52 734 measured reflections
4446 independent reflections
3695 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\rm max} = 27.5°$
$h = -27 \rightarrow 27$
$k = -27 \rightarrow 27$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.097$
$S = 1.03$
4446 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.3836P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.002$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—N1	1.4101 (15)	N2—C21	1.2757 (19)
N1—C11	1.2782 (18)	O3—N3	1.4126 (15)
O2—N2	1.4112 (15)	N3—C31	1.2859 (19)
C11—N1—O1	113.58 (11)	N2—C21—C22	117.50 (13)
N1—C11—C16	125.68 (13)	C31—N3—O3	113.06 (12)
N1—C11—C12	117.79 (13)	N3—C31—C36	125.78 (13)
C21—N2—O2	113.49 (12)	N3—C31—C32	117.16 (14)
N2—C21—C26	125.97 (13)		
O1—N1—C11—C16	1.8 (2)	N2—C21—C22—C23	−131.58 (15)
N1—C11—C12—C13	−132.61 (16)	O3—N3—C31—C36	−2.8 (2)
O2—N2—C21—C26	1.3 (2)	N3—C31—C32—C33	133.04 (15)

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1O⋯N3	0.884 (18)	1.884 (18)	2.7653 (17)	175.3 (16)
O2—H2O⋯N1	0.908 (17)	1.861 (17)	2.7632 (15)	171.9 (15)
O3—H3O⋯N2	0.89 (2)	1.89 (2)	2.7834 (17)	176.2 (18)

Refinment (II), using the structure factors of Olivateo *et al.* (2001)

Crystal data

$C_6H_{11}NO$
$M_r = 113.16$
Trigonal, $P\bar{3}$
$a = 20.9830$ (3) Å
$c = 7.6210$ (1) Å
$V = 2905.88$ (7) Å^3
$Z = 18$
$D_x = 1.164$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12992 reflections
$\theta = 1.9$–27.5°
$\mu = 0.08$ mm^{-1}
$T = 100$ (2) K
Prism, colourless
0.38 × 0.30 × 0.24 mm

Data collection

Nonius CAD-4 diffractometer
φ and ω scans
12 992 measured reflections
4440 independent reflections
3993 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.03$
$\theta_{\rm max} = 27.5°$
$h = 0 \rightarrow 27$
$k = -26 \rightarrow 23$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.089$
$S = 1.04$
4440 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 0.3995P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

For refinement (I), a first data set was collected with a rotation angle of 1° and an exposure time of 40 s per frame (248 φ scans and 433 ω scans). These data were integrated with the *HKL*2000 package (Otwinowski & Minor, 1997), resulting in 49 597 reflections in a θ range of 1.9–27.5°. Cell parameters were taken from a post-refinement of these data. A second data set of (I) was collected with a rotation angle of 1° and an exposure time of 10 s per frame (101 φ scans and 28 ω scans). These data were integrated with the *EvalCCD* package (Duisenberg *et al.*, 2003), resulting in 3137 reflections in a θ range of 1.9–15.0°. Both data sets were scaled and merged with the program *SORTAV* (Blessing, 1997). For details of the data collection of (II), see Olivato *et al.* (2001). For refinements (I) and (II), H atoms attached to O atoms were refined freely, with isotropic displacement parameters. All remaining H atoms were placed in idealized positions (C—H = 0.99–1.00 Å) and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C).

For refinement (I), data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL*2000 (Otwinowski & Minor, 1997); data reduction: *HKL*2000 and *EvalCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

For refinement (II), cell refinement: *HKL*2000 (Otwinowski & Minor, 1997); data reduction: *HKL*2000; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1726). Services for accessing these data are described at the back of the journal.

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