

## Redetermination of the twinned structure of triacetone amine monohydrate

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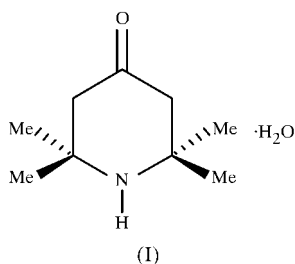
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The structure of triacetone amine monohydrate (systematic name: 2,2,6,6-tetramethylpiperidin-4-one monohydrate),  $C_9H_{17}NO \cdot H_2O$ , has been redetermined at 180 K. The compound crystallizes in space group  $P2_1/c$  with a monoclinic angle of  $90.084(3)^\circ$ . All crystals examined exhibited twinning and appeared orthorhombic, with a unit-cell volume half that of the true volume.

### Comment

Triacetone amine monohydrate, (I), has been previously reported to crystallize in the orthorhombic space group  $Pna2_1$  with four molecules in the unit cell (De Camp *et al.*, 1974). The single independent molecule of  $C_9H_{17}NO$  in this structure displays rather curious disorder of the O atom over two sites displaced either side of the position expected for the carbonyl group (Fig. 1). The structure of (I) has been redetermined and is shown to be ordered in the monoclinic space group  $P2_1/c$ , with a monoclinic angle close to  $90^\circ$  and two independent molecules. Several crystals have been examined, and in each case they exhibit twinning and appear orthorhombic, with a unit-cell volume half that of the true volume.



The orthorhombic structure of (I) reported previously by De Camp *et al.* (1974) has unit-cell parameters  $a = 9.219(1)$ ,  $b = 8.956(1)$  and  $c = 13.113(2)$  Å in space group  $Pna2_1$ . Initial examination of the crystal of (I) suggested an orthorhombic lattice with unit-cell parameters (refined against all 11 277 data)  $a = 9.0870(4)$ ,  $b = 17.7379(6)$  and  $c = 13.0508(5)$  Å, *i.e.* the true  $b$  repeat distance may be twice that reported by De

Camp. Merging of the data in the Laue group  $mmm$ , however, gave an  $R_{int}$  value of 0.120, and examination of the data revealed that the systematic absence conditions are not consistent with any orthorhombic space group. Several crystals were examined, and the same result was obtained in each case. Processing the data in Laue group  $\bar{1}$ , with the unit-cell parameters refined without constraint, showed that while  $\alpha$  and  $\beta$  did not deviate significantly from  $90^\circ$ , the angle  $\gamma$  refined to be  $89.916(3)^\circ$ . Transformation into the standard setting gives a monoclinic lattice with unit-cell parameters (refined against all 11 277 data)  $a = 9.0860(4)$ ,  $b = 13.0550(6)$  and  $c = 17.7367(6)$  Å, and  $\beta = 90.084(3)^\circ$ . The value of  $R_{int}$  for this lattice in Laue group  $2/m$  is 0.050, significantly smaller than that obtained for the orthorhombic lattice. The systematic absence conditions are consistent with space group  $P2_1/c$  and the structure was solved using *SIR92* (Altomare *et al.*, 1994) to reveal two symmetry-independent molecules.

Refinement of this structure did not proceed satisfactorily, however, stalling with  $R1 = 0.257$  for isotropic atoms prior to the addition of H atoms. This observation, together with the fact that  $\beta$  is so close to  $90^\circ$  (*i.e.* the metric symmetry appears higher than the Laue symmetry) suggests that the crystal may be twinned. Introduction of the twin law  $(100/0\bar{1}0/00\bar{1})$  immediately reduced  $R1$  to 0.160 and the refinement proceeded satisfactorily, converging with  $R1 = 0.0532$ . The scale factor for the two twin components refined to be 0.328(2). The structure is ordered, with the carbonyl groups in each independent  $C_9H_{17}NO$  molecule adopting a chemically reasonable geometry (Fig. 2). An extensive network of hydrogen bonds (see Table 1 and Fig. 3) exists within the structure.

Comparison of the monoclinic structure of (I) with that reported previously in  $Pna2_1$  by De Camp *et al.* (1974) may be made by bringing the  $2_1$  screw axes into coincidence [by transforming the orthorhombic lattice by the matrix  $(\bar{1}00/001/010)$ , followed by an origin shift of  $(0, \frac{1}{2}, 0)$ , such that the space group becomes  $Pn2_1a$ ]. The significant difference between the structures arises along the  $c$  direction; in the true monoclinic structure, molecules are related by a  $c$  glide perpendicular to  $b$  at  $y = \frac{1}{4}$ , while in the  $Pn2_1a$  structure, the corresponding molecules are related by the  $c$  lattice translation. In the orthorhombic model, therefore, two glide-related molecules are superimposed, giving rise to the observed disorder of the carbonyl group.

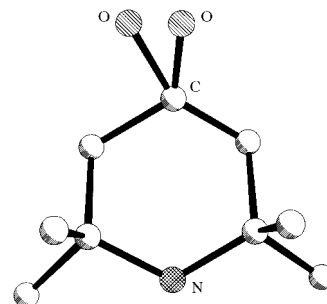
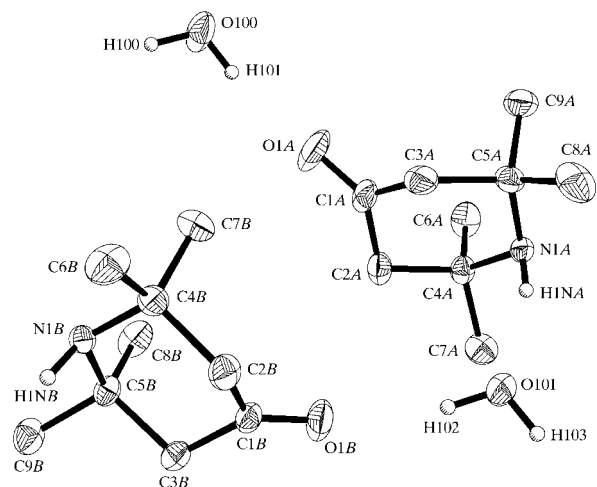
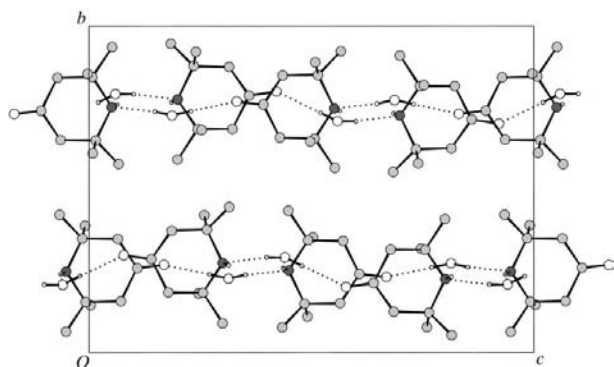


Figure 1

A view (*XP*; Sheldrick, 1993) of the disorder in the single independent molecule in De Camp's  $Pna2_1$  structure of (I) (De Camp *et al.*, 1974).



**Figure 2**  
The molecular structure and atom-labelling scheme for the two independent molecules in (I), showing displacement ellipsoids at the 30% probability level. C-bound H atoms have been omitted for clarity.



**Figure 3**  
A projection along the *a* direction showing the hydrogen-bond network in (I) (CAMERON; Watkin *et al.*, 1996). O atoms are shown as white circles, H as small white circles, C as light-grey circles and N as dark-grey circles. C-bound H atoms have been omitted for clarity.

## Experimental

The crystal of (I) was prepared by sublimation in air at room temperature, from a sample supplied by John Foulkes (Alpherantz Research, Cambridge).

### Crystal data

$C_9H_{17}NO \cdot H_2O$	$D_x = 1.094 \text{ Mg m}^{-3}$
$M_r = 173.25$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 11 277 reflections
$a = 9.0860 (4) \text{ \AA}$	$\theta = 1.0\text{--}25.0^\circ$
$b = 13.0550 (6) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 17.7367 (6) \text{ \AA}$	$T = 180 (2) \text{ K}$
$\beta = 90.084 (3)^\circ$	Block, colourless
$V = 2103.89 (15) \text{ \AA}^3$	$0.37 \times 0.30 \times 0.30 \text{ mm}$
$Z = 8$	

### Data collection

Nonius KappaCCD area-detector diffractometer	3679 independent reflections
Thin-slice $\omega$ and $\varphi$ scans	2795 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$R_{\text{int}} = 0.047$
$T_{\text{min}} = 0.934$ , $T_{\text{max}} = 0.979$	$\theta_{\text{max}} = 25^\circ$
15 306 measured reflections	$h = -10 \rightarrow 10$
	$k = -15 \rightarrow 15$
	$l = -21 \rightarrow 21$

**Table 1**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$O100\text{--}H100\cdots N1A^i$	0.89 (1)	1.98 (1)	2.861 (3)	171 (3)
$O100\text{--}H101\cdots O1A$	0.89 (1)	1.95 (1)	2.824 (3)	170 (3)
$O101\text{--}H102\cdots O1B$	0.89 (1)	2.05 (1)	2.914 (3)	166 (3)
$O101\text{--}H103\cdots N1B^{ii}$	0.89 (1)	2.01 (1)	2.888 (3)	171 (3)
$N1A\text{--}H1NA\cdots O101$	0.86 (3)	2.31 (3)	3.136 (3)	163 (2)
$N1B\text{--}H1NB\cdots O100^{iii}$	0.92 (3)	2.19 (3)	3.082 (3)	162 (2)

Symmetry codes: (i)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (iii)  $x - 1, y, z$ .

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 0.408P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.139$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
3679 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$
246 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.021 (3)

H atoms attached to C atoms were placed geometrically and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$ , where  $x = 1.5$  for methyl H atoms and 1.2 for all others. C—H distances were fixed at 0.98  $\text{\AA}$  for methyl groups and 0.99  $\text{\AA}$  for methylene groups. H atoms bound to N and O atoms were located in difference Fourier maps and their coordinates were refined and their isotropic displacement parameters set at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N or O})$ . To ensure a reasonable geometry for the water molecules, the O—H bond distances were restrained to be equivalent, with an s.u. value of 0.01  $\text{\AA}$ , and the H $\cdots$ H distances within each molecule were restrained to be 1.633 times this value, with an s.u. of 0.01  $\text{\AA}$ .

Data collection: COLLECT (Nonius, 1998); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO (Otwinowski & Minor, 1997) and SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Sheldrick, 1993); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1480). Services for accessing these data are described at the back of the journal.

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