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The low-temperature phase of di-tertbutylsilanediol

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The crystal structure of di-*tert*-butylsilanediol, $C_8H_{20}O_2Si$, has a reversible phase transition at 211 (2) K. The orthorhombic high-temperature structure has space group *Ibam*, with $Z' = \frac{1}{2}$, and shows a disordered hydrogen-bonding system. The lowtemperature structure, determined at 143 (2) K, has a twinned monoclinic cell, with space group C2/c and Z' = 2, and shows an ordered hydrogen-bonding system.

Comment

During a study of the chemical behaviour of 1,3-dichloro-1,1,3,3-tetra-tert-butyldisilazane, crystals of di-tert-butylsilanediol, (I), were obtained. Crystal structure determinations of (I) at room temperature have been reported by Graalmann et al. (1984) and Buttrus et al. (1985). Possible hydrogenbonding schemes were proposed, but no H-atom positions were reported in those studies. Due to the symmetry of the structure of (I) at room temperature, any hydrogen-bonding system must be disordered. We have remeasured (I) at a temperature of 224 K and confirmed the structure reported previously. Compound (I) crystallizes in the orthorhombic space group *Ibam*. The cell constants at 224 K are a =16.336 (2), b = 12.699 (3) and c = 10.4918 (15) Å. The molecule has m symmetry. A difference Fourier synthesis showed the H atom of the hydroxyl group to be disordered over two possible positions. Recently, this structure was also reported to occur at 173 K (Bolte & Lerner, 2001). By lowering the temperature, however, we found a reversible phase transition at 211 (2) K. We report here the low-temperature phase of (I) determined at 143 K.



On cooling (I) through the phase transition, additional reflections appear, resulting in a doubling of the *ab* diagonal of

the high-temperature Ibam cell. The low-temperature reflection data can be interpreted either by an orthorhombic C-centred unit cell or a twinned monoclinic unit cell. The structure can indeed be determined and refined in the orthorhombic space group Ccca (see Experimental); however, the resulting value of S and the residual density are larger than expected. Moreover, one tert-butyl group of this solution has displacement parameters larger than those observed for the high-temperature structure at 224 K, making this solution suspect. The structure can also be determined and refined in the monoclinic space group C2/c. In this case, the crystal is twinned and each reflection hkl coincides with reflection lkh of the twin domain. Reflections with h+k and k+l odd should be absent for both twin domains. An inspection of the measured reflections shows this indeed to be the case. The structure was refined with SHELXL97 (Sheldrick, 1997) using reflections from both twin domains simultaneously (see *Experimental*). The R values and residual density in C2/c are significantly better than those in Ccca. Thus, C2/c was adopted as the correct space group.

The low-temperature structure of (I) has two independent molecules, *A* and *B* (Fig. 1). The dimensions of both molecules are very similar. Molecule *A* shows a small deviation from the mirror-symmetrical conformation observed in the high-temperature phase; the C2–C1–Si1–C5 and C1–Si1–C5–C6 torsion angles are 178.48 (9) and $-176.01 (10)^{\circ}$, respectively, rather than 180°. Molecule *B* remains approximately mirror-symmetric; the C10–C9–Si2–C13 and C9–Si2–C13–C14 torsion angles are 179.86 (11) and 179.38 (10)°, respectively. The C–Si–C angles are rather large, at 119.20 (11) and 119.97 (11)°, due to intramolecular steric interactions between the *tert*-butyl groups. The shortest intramolecular H···H contacts are H3*B*···H7*C* 2.28 Å, H4*C*···H8*B* 2.25 Å, H11*C*···H15*B* 2.28 Å and H12*B*···H16*C* 2.27 Å.

The crystal packing of (I) at 143 K is shown in Fig. 2, which also shows the relationship between the high-temperature *Ibam* cell and the low-temperature C2/c cell. The molecules are connected by intermolecular hydrogen bonds (Table 1) to form a twisted ladder structure along the b direction. This hydrogen-bonded structure is shown in more detail in Fig. 3. Each molecule is connected by two almost straight $O-H \cdots O$ hydrogen bonds to a centrosymmetric counterpart to form a dimer. AA dimers are found at $(\frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ and symmetry-related positions, while BB dimers are found at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and symmetryrelated positions. The dimers are connected by additional O- $H \cdots O$ hydrogen bonds to form a ladder structure along **b**, with the sequence -AA-BB-AA-BB-. These latter hydrogen bonds have O-H-O angles of 148.2 (17) and 153.2 (17)°, and are less straight than the hydrogen bonds in the dimers. It is interesting to note that the Si-O-H angles are also clearly affected by the hydrogen-bonding environment, with Si1-O1-H01 113.6 (14)°, Si2-O3-H03 113.2 (17)°, Si1-O2-H02 124.2 (13)° and Si2-O4-H04 122.5 (14)°. A refinement with the X-O-H angle constrained to the tetrahedral value, as generally applied in crystal structure refinements, appears to be inappropriate in the present case. The $O1-H01\cdots O2$



Figure 1

The molecular structure of (a) molecule A and (b) molecule B of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

hydrogen bond is rotated by an angle of 38° about the *b* axis with respect to the $O3-H03 \cdots O4$ hydrogen bond, resulting in a twisted rather than a straight ladder.

In the high-temperature phase of (I), the molecules are situated about mirror planes and the hydrogen-bonded ladders have internal crystallographic symmetry ccm. Both OH groups of each molecule are symmetry related and, consequently, the H atoms must be distributed over two possible positions in each hydrogen bond. This was confirmed by our structure refinement at 224 K. Below the phase transition temperature, the crystallographic *m* symmetry is lost. Molecules A and B are tilted by angles of 3.6 and 6.8° , respectively, with respect to the (010) plane. Hydrogen bonds with ordered H-atom positions are found in the lowtemperature phase. The internal symmetry of the hydrogenbonded ladders is reduced to $\overline{1}$. The AA and BB dimers are



Figure 2

The crystal packing of (I) as a projection on [010]. The small rectangular cell with labels O', a' and b' represents the high-temperature *Ibam* cell.

related only by a pseudo-*c*-glide plane perpendicular to the *ac* diagonal. The hydrogen-bonded chain about $(\frac{1}{4}, y, \frac{1}{2})$ is related to similar chains about $(\frac{3}{4}, y, \frac{1}{2})$, $(\frac{1}{4}, y, 0)$ and $(\frac{3}{4}, y, 0)$ by the crystallographic symmetry operations C, c and n, respectively. The pseudo-mirror symmetry about $y = \frac{1}{4}$ and $\frac{3}{4}$, combined with the c-glide plane, results in pseudo-A-centring of the crystal structure.

At this point, one question still has to be answered. The cell constants do not show the structure of (I) below the phase transition temperature to be monoclinic. The lattice parameters a and c are equal, and the observed unit cell can be transformed within experimental uncertainty to a C-centred unit cell with orthorhombic geometry. As the value of the twin



Figure 3

The hydrogen-bonded ladder structure of (I), with the *b* direction from left to right. The symmetry codes are as in Table 1.

fraction is almost 0.5, the low-temperature structure of (I) may actually be orthorhombic and perhaps the best solution has not been found. To clarify this point, a smaller crystal of (I), with dimensions $0.20 \times 0.24 \times 0.30$ mm, was measured at 145 K. The twin fraction of this second crystal refined to 0.323 (1). From this additional experiment, the crystal system of the low-temperature phase of (I) is definitely shown to be monoclinic.

Experimental

A solution of 1,3-dichloro-1,1,3,3-tetra-tert-butyldisilazane (0.203 g, 0.55 mmol) in C₆D₆ (1 ml) was hydrolysed with wet air. Colourless crystals (rods) of (I) were obtained from this solution at ambient temperature (Lerner, 1994).

Crystal data	
$C_8H_{20}O_2Si$	$D_x = 1.098 \text{ Mg m}^{-3}$
$M_r = 176.33$	Mo $K\alpha$ radiation
Monoclinic, C2/c	Cell parameters from 179
a = 20.515 (3) Å	reflections
b = 10.4596 (11) Å	$\theta = 3-23^{\circ}$
c = 20.517 (3) Å	$\mu = 0.18 \text{ mm}^{-1}$
$\beta = 104.223 (13)^{\circ}$	T = 143 (2) K
$V = 4267.5 (10) \text{ Å}^3$	Block, colourless
Z = 16	$0.45 \times 0.42 \times 0.35 \text{ mm}$

Data collection

Siemens SMART CCD area-	
detector diffractometer	
ω scans	
Absorption correction: numerical	
(SHELXTL; Sheldrick, 1996)	
$T_{\min} = 0.923, T_{\max} = 0.947$	
71 887 measured reflections	
Refinement	
Refinement on F^2	
$R[F^2 > 2\sigma(F^2)] = 0.051$	
$wR(F^2) = 0.130$	
S = 1.22	
12.235 reflections	

12 235 reflections 229 parameters H atoms treated by a mixture of independent and constrained refinement 12 235 independent reflections 9107 reflections with $I > 2\sigma(I)$ $R_{int} = 0.041$ $\theta_{max} = 34^{\circ}$ $h = -31 \rightarrow 30$ $k = -16 \rightarrow 16$ $l = -31 \rightarrow 32$ $w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$

 $w = II_{[0}(F_{o}) + (0.04F) + 2P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$ $(\Delta/\sigma)_{max} = 0.001$ $\Delta\rho_{max} = 0.41 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{min} = -0.34 \text{ e } \text{Å}^{-3}$ Extinction correction: *SHELXL97*(Sheldrick, 1997)
Extinction coefficient: 0.00056 (12)

Table 1

Hydrogen-bonding geometry (Å, °).

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$O1 - H01 \cdots O2^{i}$	0.823 (13)	1.907 (13)	2.7284 (18)	176.4 (16)
$O2 - H02 \cdots O3^{ii}$	0.815 (13)	2.001 (13)	2.7530 (16)	153.2 (17)
$O3 - H03 \cdots O4^{iii}$	0.832 (16)	1.905 (17)	2.7324 (18)	173 (2)
$O4 - H04 \cdots O1$	0.826 (16)	2.058 (15)	2.7937 (16)	148.2 (17)

Symmetry codes: (i) $\frac{1}{2} - x$, $\frac{3}{2} - y$, 1 - z; (ii) x, 1 + y, z; (iii) $\frac{1}{2} - x$, $\frac{1}{2} - y$, 1 - z.

The reflections observed for (I) at 143 K are fitted perfectly by a *C*-centred orthorhombic unit cell, with a = 25.195 (4), b = 32.385 (3) and c = 10.4557 (8) Å. Systematic absences are in agreement with space group *Ccca*. R_{int} was 0.050 for orthorhombic symmetry. Structure determination and refinement in *Ccca* proceeded smoothly. The H atoms of the methyl groups were positioned geometrically and refined as riding atoms. The H atoms of the hydroxyl groups were taken from a difference synthesis and were refined with individual isotropic displacement parameters. The H atoms of the hydroxyl groups of one molecule were disordered over two possible positions. Refinement in *Ccca* converged at $wR(F^2) = 0.192$, $R[F^2 > 2\sigma(F^2)] = 0.080$ and S = 2.01, with residual density between -1.11 and $0.64 \text{ e} \text{ Å}^{-3}$. The cell constants of the twinned monoclinic structure

were determined from reflections with contributions from only a single twin domain. For the structure refinement in C2/c, the reflections were divided into four classes: reflections with h+k and k+l odd are absent and were omitted from the refinement, reflections with *h*+*k* even and *k*+l odd only have intensity contributions from domain 1, reflections with h+k odd and k+l even only have intensity contributions from domain 2, reflections with h+k and k+l even have intensity contributions from both twin domains. Refinement was performed with the HKLF 5 option in SHELXL97 (Sheldrick, 1997). The H atoms of the methyl groups were positioned geometrically and refined with fixed individual displacement parameters $[U_{iso}(H) =$ $1.5U_{eq}(C)$], using a riding model with a fixed C-H distance of 0.98 Å. The torsion angles about the C-C bonds of the methyl groups were refined. The H atoms of the hydroxyl groups were taken from a difference synthesis and were refined with individual isotropic displacement parameters. The O-H distances were restrained to 0.84(1) Å. The twin fraction refined to 0.468(1).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1561). Services for accessing these data are described at the back of the journal.

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