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The low-temperature phase of di-*tert*-butylsilanediol

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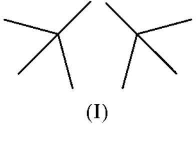
The crystal structure of di-*tert*-butylsilanediol, $C_8H_{20}O_2Si$, has a reversible phase transition at 211 (2) K. The orthorhombic high-temperature structure has space group *Ibam*, with $Z' = \frac{1}{2}$, and shows a disordered hydrogen-bonding system. The low-temperature structure, determined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



(I)

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 *C*2/*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 *SHELXL*97 (Sheldrick, 1997) using reflections from both twin domains simultaneously (see *Experimental*). The R values and residual density in *C*2/*c* are significantly better than those in *Ccca*. Thus, *C*2/*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)°, 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 *C*2/*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···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 $(\frac{1}{4},\frac{1}{4},\frac{1}{2})$ and symmetry-related positions. The dimers are connected by additional O—H···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···O2

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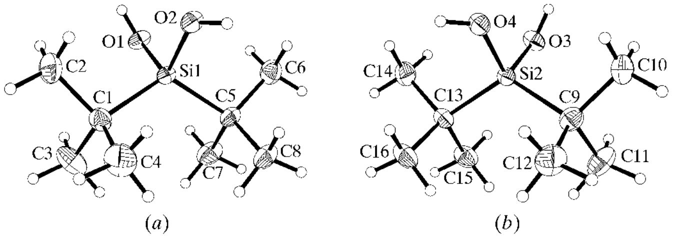

Figure 1
The molecular structure of (*a*) molecule *A* and (*b*) molecule *B* of (I) with 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

hydrogen bond is rotated by an angle of 38° about the *b* axis with respect to the O3—H03···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 low-temperature phase. The internal symmetry of the hydrogen-bonded ladders is reduced to $\overline{1}$. The *AA* and *BB* dimers are 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.

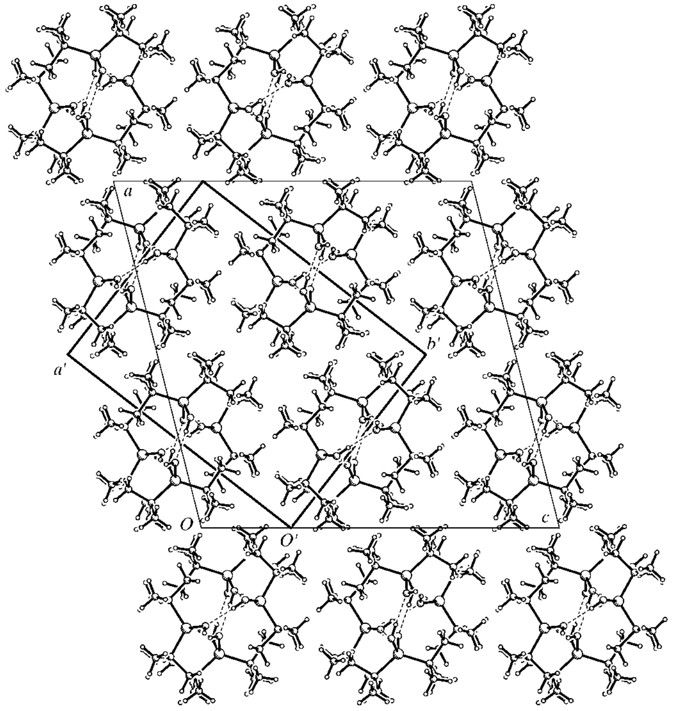

Figure 2
The crystal packing of (I) as a projection on [010]. The small rectangular cell with labels *O*′, *a*′ and *b*′ represents the high-temperature *Ibam* cell.

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 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 × 0.24 × 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.

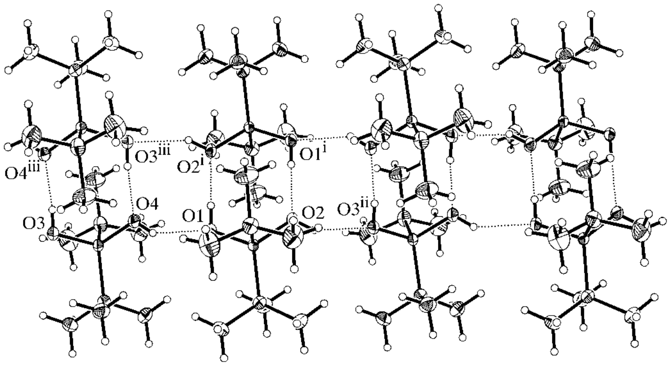

Figure 3
The hydrogen-bonded ladder structure of (I) , with the *b* direction from left to right. The symmetry codes are as in Table 1.

Experimental

A solution of 1,3-dichloro-1,1,3,3-tetra-*tert*-butyldisilazane (0.203 g, 0.55 mmol) in C_6D_6 (1 ml) was hydrolysed with wet air. Colourless crystals (rods) of (I) were obtained from this solution at ambient temperature (Lerner, 1994).

Crystal data

$C_8H_{20}O_2Si$
$M_r = 176.33$
Monoclinic, *C*2/*c*
$a = 20.515$ (3) Å
$b = 10.4596$ (11) Å
$c = 20.517$ (3) Å
$\beta = 104.223$ (13)°
$V = 4267.5$ (10) Å^3
$Z = 16$

$D_x = 1.098$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 179 reflections
$\theta = 3$–23°
$\mu = 0.18$ mm^{-1}
$T = 143$ (2) K
Block, colourless
0.45 × 0.42 × 0.35 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

12 235 independent reflections
9107 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 34°$
$h = -31 \rightarrow 30$
$k = -16 \rightarrow 16$
$l = -31 \rightarrow 32$

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
229 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00056 (12)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01···O2$^{\rm i}$	0.823 (13)	1.907 (13)	2.7284 (18)	176.4 (16)
O2—H02···O3$^{\rm ii}$	0.815 (13)	2.001 (13)	2.7530 (16)	153.2 (17)
O3—H03···O4$^{\rm iii}$	0.832 (16)	1.905 (17)	2.7324 (18)	173 (2)
O4—H04···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*. $R_{\rm int}$ 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 e 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 *C*2/*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 *SHELXL*97 (Sheldrick, 1997). The H atoms of the methyl groups were positioned geometrically and refined with fixed individual displacement parameters [$U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(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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