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The unusual phases of anhydrous and hydrated pinacol

Xiang Hao, Sean Parkin and Carolyn Pratt Brock*

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

Correspondence e-mail: cpbrock@uky.edu

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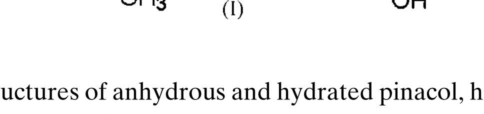
The structure of highly twinned pinacol (2,3-dimethyl-2,3-butanediol) monohydrate, the existence of which has been known since 1922, has been determined, and the structures of anhydrous pinacol and its two other known hydrates have been reinvestigated. All the phases are unusual. The anhydrous phase [Jeffrey & Robbins (1978). *Acta Cryst.* B**34**, 3817–3820] is exceptional among molecular crystals in having molecules located on three different symmetry sites (1, $\overline{1}$ and 2). A hexagonal form of pinacol originally described as a second polymorph [Dahlqvist & Sillanpää (2000). *J. Mol. Struct.* **524**, 141–149] has been shown to be a solvate of uncertain composition that is very loosely packed. Pinacol hexahydrate, which was originally reported as tetragonal and highly disordered [Kim & Jeffrey (1970). *J. Chem. Phys.* **53**, 3610–3615], appears to be described better as having an orthorhombic structure that is both disordered and twinned; the diffraction pattern at 90 K shows structured diffuse scattering that suggests short-range correlations of disordered molecules. The occurrence of this unusual set of structures is attributed to the combination of the hydrogen-bonding requirements of the pinacol molecule with its small size and limited conformational flexibility.

1. Introduction

Pinacol (2,3-dimethyl-2,3-butanediol) appears to be an unexceptional small molecule that has two important conformers (*anti* and *gauche*) of similar energy (Dahlqvist *et al.*, 1998). Both conformers of this *vicinal* diol can be expected to form intermolecular O—H···O bonds in the solid state (Brock, 2002). If pinacol behaved like most other small molecules a single low-energy conformation would be present in the crystal. Since the molecule can conform to inversion symmetry, the molecule would lie on a $\overline{1}$ site (Yao *et al.*, 2002; Pidcock *et al.*, 2003), in which case the conformation would be *anti*. The space group would be expected to be monoclinic or triclinic (Brock & Dunitz, 1994, and references therein). In any hydrate the ratio of water molecules to pinacol molecules would be low.



(I)

The structures of anhydrous and hydrated pinacol, however, confound expectations about how molecules should pack. Anhydrous pinacol is reported to crystallize (Jeffrey & Robbins, 1978) in *C*2/*c* with two conformers (*gauche* and *anti*) located on three kinds of symmetry sites (1, 2 and $\overline{1}$), and with

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the centrosymmetric molecule disordered over two sites in a 3:1 ratio. The structure has no obvious pseudosymmetry. The two other pinacol and pinacol hydrate structures in the Cambridge Structural Database (Allen, 2002; hereafter the CSD) are described in high-symmetry (tetragonal and hexagonal) space groups. The hydrate is a hexahydrate. The hexagonal space group is chiral.

The phase diagram for water and pinacol ($T_{\rm fus}$ = 314.2 K) was determined over 80 years ago (Pushin & Glagoleva, 1922) by careful cooling of solutions of highly purified pinacol and water (see Fig. 1). That diagram shows that the hexahydrate has a surprisingly high melting point ($T_{\rm fus}$ = 318.6 K) and that there is a lower melting ($T_{\rm fus}$ = 314.4 K) monohydrate. The structure of the monohydrate has never been published, although attempts to determine it were discussed in an M.Sc. thesis (O'Connor, 1969). Eutectic points (302.6 K at $X_{\rm pinacol}$ = 0.80, and 313.6 K at $X_{\rm pinacol}$ = 0.385) were identified between each pair of phases. The hexagonal phase described by Dahlqvist & Sillanpää (2000) as melting at 300–302 K was not observed by Pushin & Glagoleva (1922), presumably because it is metastable.

In pinacol hexahydrate (Kim & Jeffrey, 1970) *anti* conformers bridge sheets formed from pentagons of water molecules. We thought it possible that these crystals ($P4_2/mnm$; Z' = 1/8; mmm symmetry imposed) might actually be twins, with the individuals having an ordered, orthorhombic structure, especially if the structure were studied at low temperature.

Although the hexagonal structure ($P6_5$, Z' = 2) has been described as a second polymorph of anhydrous pinacol (Dahlqvist & Sillanpää, 2000), the model of the structure contains large, empty channels that must be filled, probably with water molecules.

As these structures are so unusual (high Z'; high symmetry; high ratio of water to pinacol) and because the available hardware and software are so much more advanced than when most of these structures were investigated, we decided to look at this system again.

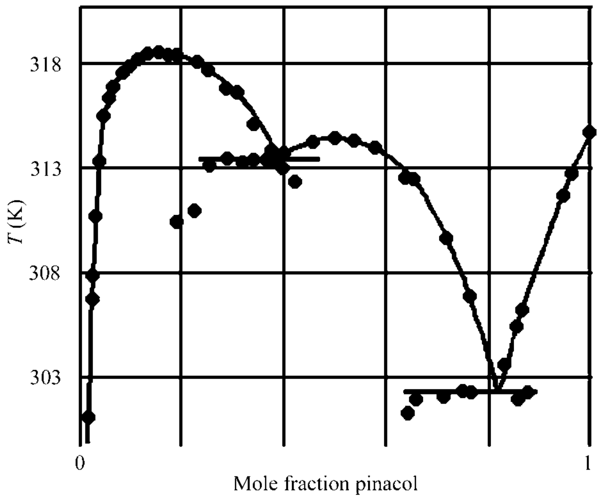

Figure 1
The phase diagram of pinacol and water near P = 1 atm redrawn from Fig. 2 of Pushin & Glagoleva (1922).

2. Experimental

2.1. Crystallographic experiments

Crystals were grown at room temperature from pinacol/water solutions and by sublimation. Crystals were mounted in oil at room temperature and cooled rapidly (within several seconds). Data for the mono- and hexahydrate were measured at 90 K. Data for the hexagonal crystals were measured at 173 K rather than at 90 K, because after a new low-temperature system that would reach 90 K was installed we were no longer able to find a suitable crystal. Data for anhydrous pinacol were measured at both 173 and 90 K.

After the orientation matrix for each crystal had been determined (Otwinowski & Minor, 1997), the data in the frames were transformed using the PRECESSION routine in *COLLECT* (Nonius, 2000) to give undistorted views of reciprocal-lattice slices $nk\ell$, $hn\ell$ and hkn, n = 0–3. The diffraction pattern of the anhydrous phase was normal, but slices for the other phases had unusual features. The slices for the monohydrate show features that suggest twinning (wide spots of surprisingly similar intensity), the intensities for the hexagonal phase fall off rapidly with scattering angle, and there is significant diffuse scattering in the diffraction pattern of the hexahydrate.

Crystal data are given in Table 1; information about the hydrogen bonds is given in Tables 2 and 3. The displacement ellipsoids and numbering schemes are shown in Fig. 2; the structures are illustrated in Figs. 3–6. All other structural information, including pictures of all the crystals except for the hexagonal phase, has been deposited.[1] Methyl groups were idealized but free to rotate (AFIX 137); $U_{\rm iso}$ values for methyl H atoms were $1.5U_{\rm iso}$ for the methyl C atom. Comments specific to individual structures follow.

2.1.1. Anhydrous pinacol. Crystals were grown by sublimation near room temperature in a sealed vial set on a warm surface. The very attractive, multifaceted crystals look monoclinic. Refinements from the structure of Jeffrey & Robbins (1978) were straightforward, but the disorder they reported at room temperature was not found at either 173 or 90 K. The hydroxyl H atoms could be located in difference Fourier syntheses and refined freely (see Table 2). The $U_{\rm iso}$ values for the hydroxyl H atoms ranged from 0.037 (5) to 0.045 (5) Å^2 at 90 K and were about 30% larger at 173 K.

2.1.2. Pinacol monohydrate. A few drops of water were added to a sample of anhydrous pinacol; the vial was then resealed and left at room temperature for several weeks. At the end of that time the liquid water had disappeared and some new crystals that were thick laths were found.

The diffraction pattern for this crystal form 'looks' tetragonal (see upper half of Fig. 7), but the lengths of the cell edges were found to be 14.688 (3), 14.727 (3) and 15.244 (3) Å; a and b differ by 0.3%. More importantly, when viewed with a polarizing microscope down the apparent fourfold axis (which is the direction in which the crystals grow longest) the crystals

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[1] Supplementary material for this paper is available from the IUCr electronic archives (Reference WS5034). Services for accessing the archive are described at the back of the journal.

Table 1
Crystal data.

	Anhydrous (173 K)	Anhydrous (90 K)	Monohydrate (90 K)	Hexahydrate (90 K)	Hexagonal (173 K)
Crystal data					
Chemical formula	$C_6H_{14}O_2$	$C_6H_{14}O_2$	$C_6H_{14}O_2{\cdot}H_2O$	$C_6H_{14}O_2{\cdot}6H_2O$	$C_6H_{14}O_2{\cdot}0.5H_2O$
M_r	118.17	118.17	136.19	226.27	127.18
Cell setting, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Monoclinic, *P*2/*n*	Orthorhombic, *Pnnm*	Hexagonal, $P6_522$
a, *b*, *c* (Å)	16.360 (3), 16.219 (3), 10.942 (2)	16.333 (3), 16.145 (3), 10.916 (2)	10.582 (2), 7.3637 (15), 10.587 (2)	6.308 (2), 6.321 (2), 15.759 (3)	14.696 (2), 14.696 (2), 13.686 (3)
α, β, γ (°)	90.00, 90.96 (3), 90.00	90.00, 90.92 (3), 90.00	90.00, 92.13 (3), 90.00	90.00, 90.00, 90.00	90.00, 90.00, 120.00
V (Å^3)	2903.0 (9)	2878.1 (9)	824.4 (3)	628.4 (3)	2559.8 (7)
Z	16	16	4	2	12
D_x (Mg m^{-3})	1.082	1.091	1.097	1.196	0.990
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2804	6281	5559	1360	3031
θ range (°)	1.0–27.5	1.0–27.5	1.0–27.5	1.0–27.5	1.0–25.4
μ (mm^{-1})	0.08	0.08	0.09	0.11	0.08
Temperature (K)	173 (2)	90.0 (2)	90.0 (2)	90.0 (2)	173 (2)
Crystal form, color	Block, colorless	Block, colorless	Block, colorless	Block, colorless	Needle, colorless
Crystal size (mm)	0.20 × 0.15 × 0.10	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.15	0.20 × 0.20 × 0.15	0.50 × 0.10 × 0.10
Data collection					
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Data collection method	ω scans at fixed χ = 55°	ω scans at fixed χ = 55°	ω scans at fixed χ = 55°	ω scans at fixed χ = 55°	ω scans at fixed χ = 55°
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.984	0.977	0.975	0.978	0.964
$T_{\max}$	0.992	0.984	0.987	0.984	0.993
No. of measured, independent and observed reflections	5431, 3333, 2173	11 933, 3297, 2561	2125, 2125, 1666	3531, 734, 559	4442, 1121, 836
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.027	0.033	0.098	0.039	0.026
$\theta_{\max}$ (°)	27.5	27.5	25.0	27.5	22.5
Range of *h*, *k*, *l*	$-21 \Rightarrow h \Rightarrow 21$ $-21 \Rightarrow k \Rightarrow 14$ $-14 \Rightarrow l \Rightarrow 14$	$-21 \Rightarrow h \Rightarrow 21$ $-20 \Rightarrow k \Rightarrow 20$ $-14 \Rightarrow l \Rightarrow 14$	$-12 \Rightarrow h \Rightarrow 12$ $-8 \Rightarrow k \Rightarrow 8$ $-12 \Rightarrow l \Rightarrow 12$	$-8 \Rightarrow h \Rightarrow 8$ $-7 \Rightarrow k \Rightarrow 7$ $-20 \Rightarrow l \Rightarrow 16$	$-15 \Rightarrow h \Rightarrow 15$ $-13 \Rightarrow k \Rightarrow 13$ $-14 \Rightarrow l \Rightarrow 14$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.048, 0.128, 1.07	0.040, 0.107, 1.04	0.053, 0.123, 1.05	0.036, 0.094, 1.03	0.072, 0.214, 1.05
No. of reflections	3333	3297	2125	734	1121
No. of parameters	170	169	97	87	95
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.8893P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 1.4237P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.165P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.1463P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1531P)^2 + 0.2175P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.0001	<0.0001	0.001	<0.0001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.25, −0.19	0.29, −0.21	0.20, −0.23	0.28, −0.14	0.25, −0.16
Extinction method	*SHELXL*	None	None	None	None
Extinction coefficient	0.0041 (7)	–	–	–	–

Computer programs used: *COLLECT* (Nonius, 2000), *SCALEPACK*, *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXD* (Schneider & Sheldrick, 2002), *SHELXL*97 (Sheldrick, 1997*b*), *XP* in Siemens *SHELXTL* (Sheldrick, 1994), and local procedures.

extinguish normally rather than being dark at all orientations as the crystals would be if they were tetragonal. Finally, the agreement factor $R_{\rm sym}$ for the averaging of 5538 reflections in tetragonal symmetry is 0.193, but the factor decreases to 0.117 for the averaging of 5392 reflections in orthorhombic symmetry.

The crystallographic software found the space-group absences to be consistent with the orthorhombic group *Ibca*, but no structure solution could be found in that group.

The precession projections (see Fig. 7) showed that the diffraction spots are wide in all directions and that the widths of the spots appear to increase with scattering angle. The

Table 2
Hydrogen-bond parameters (Å, °) for anhydrous pinacol.

	O—H	H···O	O···O	O—H···O
At 90 K				
O1—H11···O3	0.83 (2)	2.01 (2)	2.792 (2)	156 (2)
O3—H31···O2^{i}	0.80 (2)	2.01 (2)	2.768 (2)	156 (2)
O2—H21···O4^{i}	0.80 (2)	1.99 (2)	2.780 (2)	169 (2)
O4—H41···O1	0.86 (2)	1.93 (2)	2.766 (2)	166 (2)
At 173 K				
O1—H11···O3	0.85 (2)	2.01 (2)	2.804 (2)	156 (2)
O3—H31···O2^{i}	0.83 (2)	2.00 (2)	2.774 (2)	156 (2)
O2—H21···O4^{i}	0.84 (2)	1.97 (2)	2.789 (2)	166 (2)
O4—H41···O1	0.90 (2)	1.89 (2)	2.775 (2)	168 (2)

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

Table 3
O···O distances (Å) for pinacol hydrates.

Pinacol monohydrate at 90 K			
O1—H1···O3	2.737 (3)	O2—H2···O3^{i}	2.766 (3)
O3—H32···O1^{ii}	2.740 (3)	O3—H31···O2	2.680 (3)
Hexagonal phase at 173 K			
O1···O1^{iii}	2.830 (5)	O2···O2^{iv}	2.699 (6)
O1···O2^{v}	2.751 (4)		
pinacol hexahydrate at 90 K			
O1···O2	2.815 (2)		
O2···O2^{vi}	2.799 (3)	O3···O2	2.783 (1)

Symmetry codes: (i) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (ii) $2-x, 1-y, 1-z$; (iii) $1-y, 1-x, \frac{13}{6}-z$; (iv) $1-x+y, y, \frac{3}{2}-z$; (v) $x, x-y, \frac{11}{6}-z$; (vi) $-x, -y, z$.

observed absence conditions are abnormal (*e.g.* if one index is odd, the reflection is absent if either of the other two indices is zero). The value (0.89) of $|E^2-1|$ would be consistent with a centrosymmetric structure that is twinned. The $R_{\rm int}$ values for the averaging of reflections for the three choices of an *I*-centered monoclinic cell (with a monoclinic angle very near 90°) are 0.102 (3574 reflections), 0.098 (3572 reflections) and 0.104 (3577 reflections). It seemed probable that the symmetry was actually monoclinic with **b** unique.

The structure was finally solved using the program *SHELXD* (Schneider & Sheldrick, 2002), which has the ability to handle twinned crystals. A good model was eventually found in the monoclinic group *I*2/*a*. The structure is doubly twinned so that reflections (h,k,ℓ), ($-k,h,\ell$), ($-h,-k,\ell$) and ($k,-h,\ell$) (or their symmetry-equivalent counterparts) all overlap. This overlap is consistent with an approximate four-fold axis parallel to **c** (where **b** is the unique monoclinic axis). The 'twin' fractions for the domains that correspond to the ($-k,h,\ell$), ($-h,-k,\ell$) and ($k,-h,\ell$) reflections were determined to be 0.186 (2), 0.287 (2) and 0.179 (2); the fraction corresponding to the (h,k,ℓ) reflections is therefore 0.348.

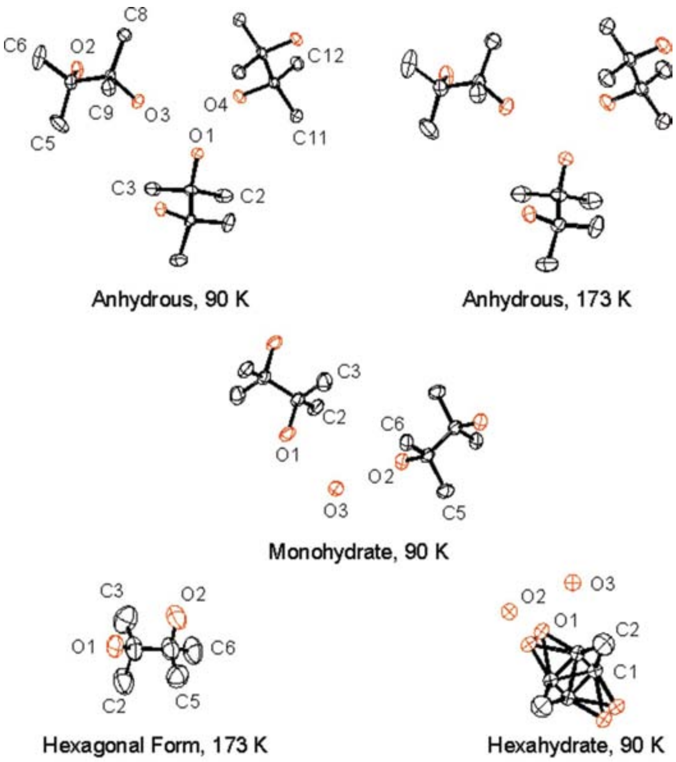

Figure 2
Drawings of all the molecules reported in this study. Ellipsoids have been drawn at the 50% probability level and H atoms have been omitted. The atom-numbering schemes are shown; the numbers of the backbone C atoms are 1 and 2 less than the numbers of the attached methyl C atoms. In the case of imposed symmetry only the unique atoms have been labeled.

The refinement in *I*2/*a* was plagued by very large correlations that suggested the presence of inversion centers within the two independent pinacol molecules and relating the two independent water molecules. An examination of the crystal packing revealed what seemed to be an almost perfect translation of **b**/2. The true $k = 2n+1$ reflections (*i.e.* reflections of a single individual) were calculated to be 200–500 times weaker (depending on the scattering angle) than the true $k = 2n$ reflections. The pseudomerohedral twinning described above, however, mixes up the **a** and **b** directions so that $h = 2n$ reflections and $k = 2n+1$ reflections are superimposed. The resulting superposition causes the h odd reflections of the twinned crystal to be weaker than they would be in an untwinned crystal and the k odd reflections to be stronger.[2]

A very careful examination of the crystal packing using the program *Mercury* (Bruno *et al.*, 2002) led us to suspect that the true space group might be *P*2/*n*. The transformation matrix relating the unit-cell vectors and the Miller indices in the equation $a_{P2/n} = Ma_{I2/a}$ would then be $(\frac{1}{2}\,0\,\frac{1}{2}\,/\,0\,-\frac{1}{2}\,0\,/\,\frac{1}{2}\,0\,-\frac{1}{2})$ and the four contributing twin-component reflections for the *P*2/*n* cell would be $(h+\ell)/2, -k/2, (h\,\ell)/2, (h-\ell)/2, k/2, (h+\ell)/2, (-k-\ell)/2, h/2, (-k+\ell)/2$ and $(-k+\ell)/2\;-h/2\;(-k-\ell)/2$, where h, k and ℓ refer to the original *I*2/*a* cell. If h, k and ℓ (*I*2/*a* axes) are all even then four different reflections would contribute to each measured composite reflection. If h or k is

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[2] The pseudomerohedral twinning also mixes up the absences for the *a* glide plane ($h0\ell$, $\ell = 2n+1$, which means that h odd is also absent because of the *I* centering) with the $0k\ell$, k and $\ell = 2n+1$ reflections. Since all the k odd reflections are so weak, the reflection superposition results in apparent absences for both $h0\ell$ and $0k\ell$. The weak k-odd reflections also lead to the apparent absence condition $hk0$, k odd (and thus also h odd because of the centering), so there are apparent glide planes perpendicular to **c** also. Hence the apparent space group *Ibca*.

odd (in which case ℓ must be odd because of the I centering), then only two reflections would contribute to each composite reflection because the other two contributors have half-integral indices. If both h and k are odd ($I2/a$ axes), then all four indices in the $P2/n$ cell are half-integral and the intensity of the composite 'reflection' should be zero. Of the 953 reflections with h and k ($I2/a$ axes) both odd, only 29 have $I > 2\sigma(I)$ and only 4 have $I > 3\sigma(I)$.

After the appropriate transformation the structure was refined successfully in the space group $P2/n$ (see Table 1). There are two independent pinacol molecules, each located on an inversion center, and one independent water molecule.

An early attempt to solve this structure (O'Connor, 1969) resulted in room-temperature, tetragonal cell dimensions smaller by factors of two than those we observed. The absences pointed to the space group $P4_2$. We suspect that the weak reflections having h or k odd were missed and that the ℓ odd reflections were missed because they can only occur (because of the I centering) in combination with h or k odd. Nevertheless, the basic hydrogen-bonding pattern suggested was correct, perhaps because of the analogy made with the structure of pentamethylethanol (Pachler & von Stackelberg, 1963; refcode TMBUOL).

2.1.3. Hexagonal phase. A few crystals of the hexagonal phase were found in the vial in which pinacol had been sublimed (see above). The crystals are very fine needles that are elongated along **c**.

The structure of the hexagonal form of pinacol was reported by Dahlqvist & Sillanpää (2000), who grew their crystals from cyclohexane. These authors reported the structure as unsolvated, even though there are very large channels (radius of slightly more than 5 Å between van der Waals surfaces) that run along **c**. The space group was given as $P6_5$ with $Z' = 2$, but we find that there are twofold rotation axes perpendicular to **c** because $R_{\rm sym}$ for our data is 0.028 for the averaging of 1444 reflections in $P6/m$ and 0.029 for the averaging of 2088 reflections in $P6/mmm$. For the sake of consistency with the previous report we have described the crystal in the space group $P6_522$ rather than in $P6_122$, but we were unable to distinguish between the 6_1 and 6_5 axes. The value of Z' is 1 rather than 2. We also find significant helices of electron density (*ca* 0.9 e Å^{-3}) in the channels, although this density is diffuse rather than localized.

The relatively small crystals (see Table 1) scattered so weakly at 173 K that including data with $2\theta > 45°$ ($\sin\theta/\lambda > 0.538$ Å^{-1}) in the refinement was counterproductive.

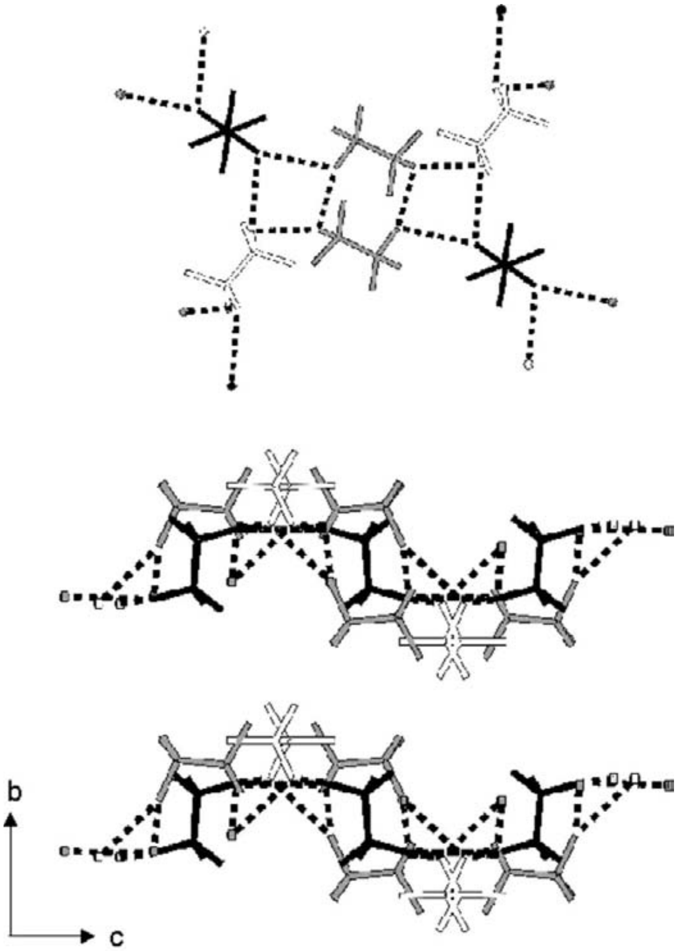


Figure 3
Upper diagram shows the basic building block of a layer of the anhydrous pinacol structure. Molecule 1 (lightest) lies on a twofold axis and molecule 3 (darkest) lies on an inversion center; the third molecule (2) lies on a general position. The lower diagram shows the stacking of the layers along **b**.

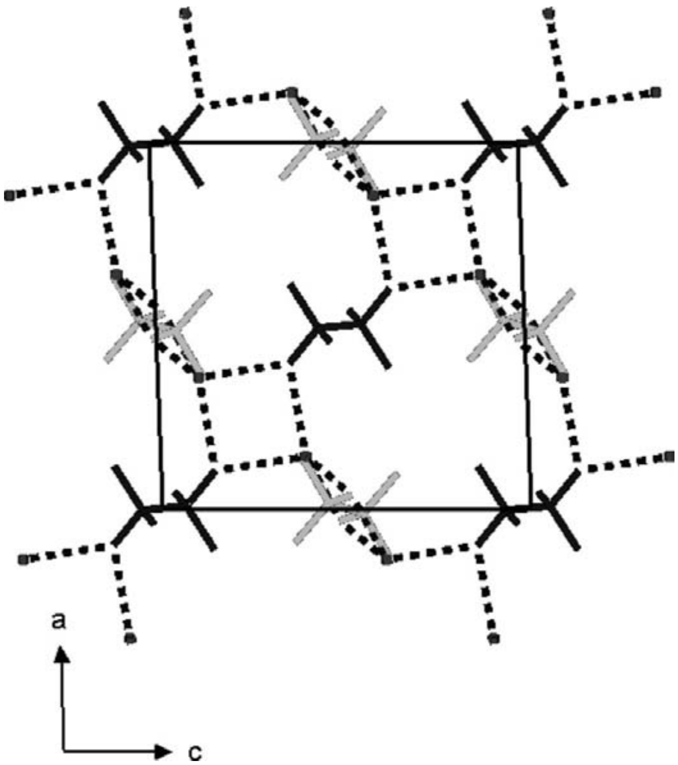
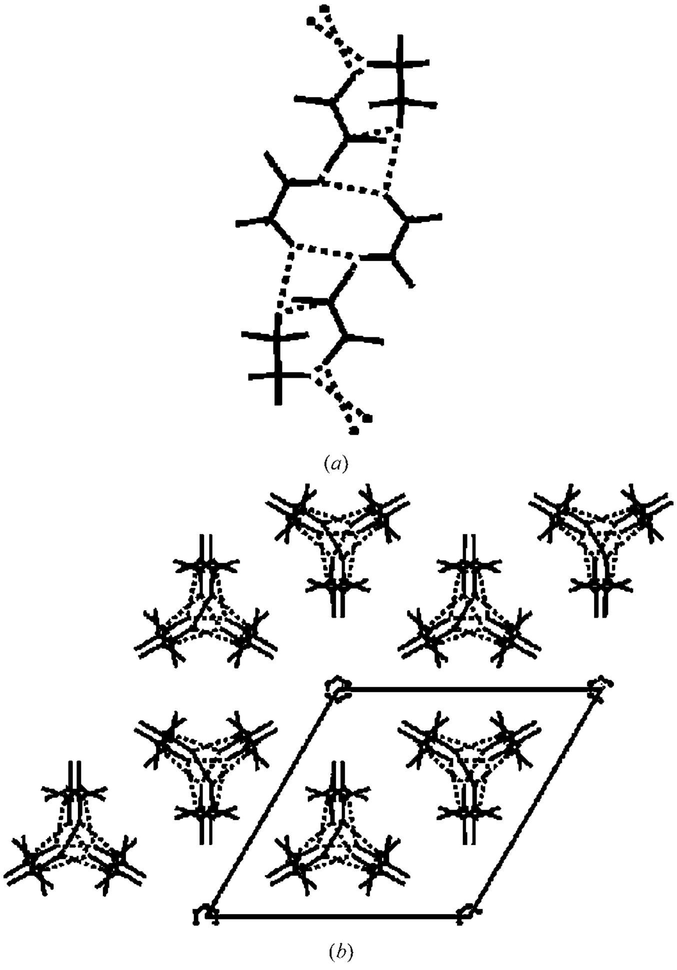


Figure 4
A projection down **b** of the pinacol monohydrate structure. Both pinacol molecules lie on inversion centers. The $R_4^4(8)$ hydrogen-bonded rings including molecule 1 (lighter; chains along [010]) lie on inversion centers, while the $R_4^4(8)$ rings including molecule 2 (darker; chains along [101]) lie on twofold axes.

The space group requires that the hydroxyl H atoms each be located at two positions that have equal occupancies (see below). These H atoms were placed in idealized positions, then refined under the restraints that all O—H distances be equal [final value 0.87 (5) Å] and that the H1*A*···H1*B* and H2*A*···H2*B* distances be equal. The $U_{\rm iso}$ values for hydroxyl H atoms were fixed at 0.12 Å^2.

We cannot be certain about the composition of this phase, although it seems impossible that the channels are empty, especially given the electron density observed. The channels are probably filled by some combination of H_2O, O_2 and N_2 molecules (see *e.g.* Görbitz, 2002). Each of these three molecules has a volume (Hofmann, 2002; Mighell *et al.*, 1987) of 20–24 Å^3. If the molecule is H_2O and if the molecules in a channel are related by a 6_1 (or 6_5) axis, then the compound is pinacol hemihydrate and the ratio $V_{\rm obs}/V_{\rm pred}$ = 1.13. It is our experience that this value is very large for a structure determined at 173 K, even if the packing is loose and the structure has many O—H···O bonds. The program *PLATON* (Spek, 2003) also issues a warning about the presence of too much empty space in the hemihydrate. If there are 12 water molecules in the channel or 12 O_2 or N_2 molecules, then the ratio $V_{\rm obs}/V_{\rm pred}$ would be 1.06–1.07, which is still large for a low-temperature structure but which is closer to expectations.


(*a*)

(*b*)

Figure 5
Diagram of part of (*a*) the pinacol helix and (*b*) of the overall packing in the hexagonal phase. The contents of the large channels (*e.g.* at 0, 0, 0) are not well determined.

The SQUEEZE routine in *PLATON* (Spek, 2003) has proven to be a useful tool for removing the contributions of disordered solvent from diffraction intensities in order to improve the refinement of ordered parts within a structure. Although no substantial improvements to the geometry of the pinacol molecule were apparent upon the application of SQUEEZE, the solvent-accessible voids along **c** were easily identified. On the assumption that the electron density within the channels is due to water, both the SQUEEZE procedure and a difference map suggest an upper limit of six water molecules per cell for this crystal. This value is consistent with the structure being a hemihydrate, but we have no information on whether this crystal suffered loss of solvent from its channels during crystal growth, storage or handling.

The conventional model for this structure that gave the best refinement included one half-occupancy O atom in the channel, but the $U_{\rm iso}$ value is very large [0.63 (3) Å^2] and the O···O distance [2.352 (11) Å] is too short. Again, water molecules may have been lost between the time the crystal was grown and the time the data were measured.

A search of the CSD for trigonal and hexagonal structures containing water molecules turned up a dozen structures having water molecules in channels extending along **c**. Few of these structures provide really satisfactory descriptions of the channel contents; in most cases the O···O distances are short, the occupancy factors are low or there is too much empty space. The modeling of such structures is clearly problematic.

2.1.4. Pinacol hexahydrate. Water and pinacol were placed together in a vial, which was allowed to stand at room

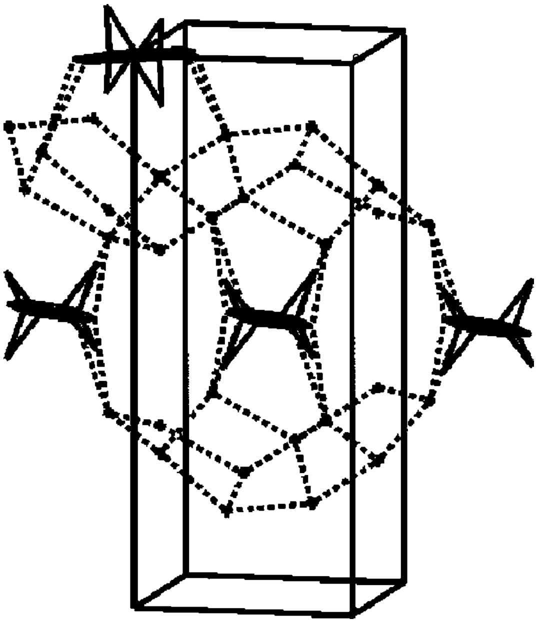
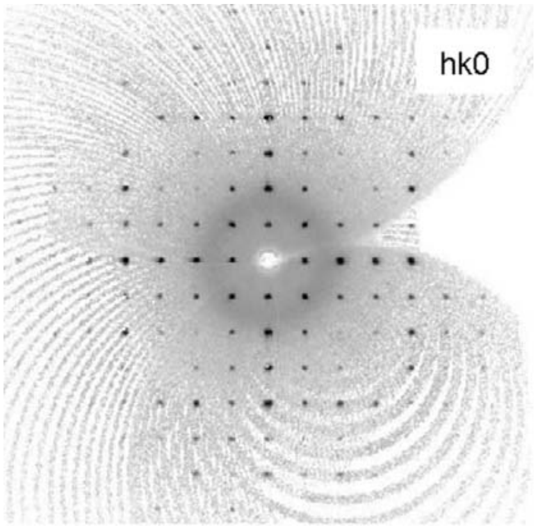


Figure 6
Part of the structure of pinacol hexahydrate. The *c* axis is vertical.

temperature for some weeks. At the end of that time crystals that are thick plates with perpendicular edges were found in equilibrium with a solution. When the crystals were viewed along the plate normal under the polarizing microscope they were dark at all rotation angles, but not quite as dark as true high-symmetry crystals (*e.g.* cubic NaCl) would be. Only some of the pinacol crystals, however, looked tetragonal. While some had square cross sections, others had sets of small faces that are inconsistent with 4 or $\overline{4}$ symmetry.

Initial refinements used the space group $P4_2/mnm$ reported by Kim & Jeffrey (1970) and started from their room-temperature coordinates. This space group requires that the pinacol molecule be disordered over a site of *mmm* symmetry. The mirror perpendicular to **c** is likely to be real because it generates no disorder and because the atomic displacements perpendicular to the mirror (as measured by the atomic displacement parameters) are within normal limits. We then looked at the other tetragonal ($P\overline{4}n2$; $P4_2nm$) and orthorhombic (*Pnnm*; *Pnn*2) space groups that have the same extinctions as $P4_2/mnm$. Of these groups only *Pnnm* allows the mirror symmetry perpendicular to **c** without requiring any disorder. If the space group were *Pnnm* then pseudomerohedral twinning could explain the apparent tetragonal symmetry of the diffraction pattern.



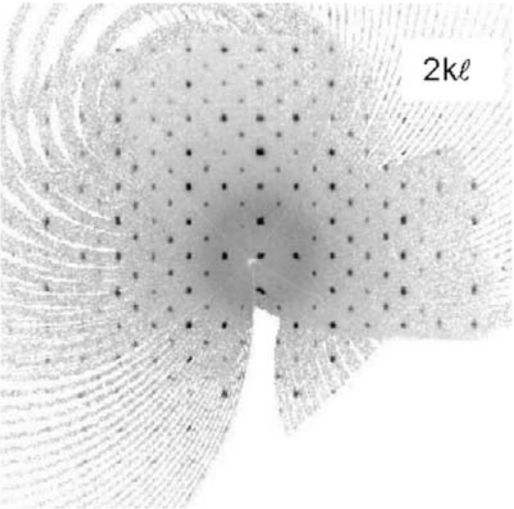


Figure 7
Scattering in the *hk*0 (upper picture) and 2*k*ℓ (lower picture) layers of pinacol monohydrate. The symmetry appears to be tetragonal and the spots are large.

The precession-like projections (*i.e.* reciprocal-lattice slices) of the tetragonal diffraction pattern (given in Fig. 8 and in the supplementary material) show very pronounced streaking (or diffuse scattering) along the {110} directions in planes (*hkn*) for the four projections calculated (*n* = 0–3). The diffuse scattering is much weaker in (*hk*1) than in (*hk*0) or (*hk*2), but is still obvious. We found no significant non-Bragg scattering in the planes (*hn*ℓ) or (*nk*ℓ), *n* = 0–3.

The diffraction maxima do appear to be wider in the directions perpendicular to **c*** than along it. That observation would be consistent with pseudomerohedral twinning resulting from interchange of the **a** and **b** axes. The observations made using a polarizing microscope (see above) are also consistent with the presence of twinning.

We investigated structural models that included disorder and/or pseudomerohedral twinning because the presence of diffuse scattering suggests that the correlation length is intermediate between the short correlation lengths typical of disorder and the much longer correlation lengths typical of twinning. Our choice for the most satisfactory model (see Table 1) is in the space group *Pnnm* with both disorder [one occupancy factor is 0.572 (4)] and twinning [one twin fraction is 0.32 (2)]. The difference of these two refined values from 0.5 is one reason for preferring the refinement in the orthorhombic group.

2.2. Searches of the CSD

Final searches were made using Version 5.26 (November 2004) of the CSD along with the February and May 2005

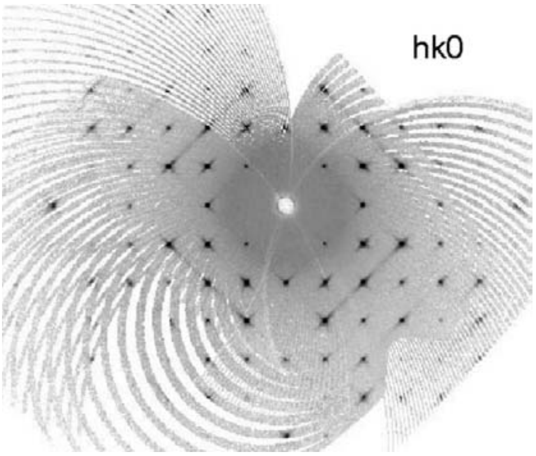


Figure 8
Scattering in the *hk*0 layer of pinacol hexahydrate. The **a*** and **b*** axes are horizontal and vertical.

updates. There is no simple way to find all structures with molecules on three different kinds of sites. A list of space groups containing three types of sites was compiled from Vol. A of *International Tables* (Hahn, 1983). Space groups were grouped so that the number of hits could be limited by conditions on Z' (*e.g.* $Z' = 2$ for $C2/c$ and $0.625 \le Z' \le 2$ for $P4/nnc$), although exact limits were not set for every space group. Hits were screened individually. For many of the hits the combination of the space group and the Z' value was impossible for molecules (or ions) that should lie on three types of symmetry sites. For a number of others it was clear that the molecules could not conform to the necessary symmetry operations (*e.g.* both $\bar{1}$ and 2). The few remaining hits were examined with the program *Mercury* (Bruno *et al.*, 2002).

A few hits corresponded to network structures (one-, two- or three-dimensional) and were therefore rejected because the focus of this study is the packing of discrete molecules. Highly disordered structures were also excluded.

3. Results

3.1. Database searches

Only six reliable structures were found (other than pinacol) that have molecules on three different types of sites. All the structures are ionic; in most either all the cations or all the anions lie on general positions. The structures found are DAMCEA (Shin *et al.*, 2004), FUCJIT (Nagao *et al.*, 1987), QAZFUS (Vamvounis *et al.*, 2000), TUYLAA (Bator *et al.*, 2001), and the isostructural pair VISYUR and VISZAY (Zúñiga *et al.*, 1991). Three of the six structures are reported to have phase transitions at higher temperatures.

The very low-temperature phase of CD_4 is reported to have the space group $P\bar{4}m2$ with molecules on nine sites of symmetries 1, m and $mm2$ (ZZZWEQ14; Prokhvatilov & Isakina, 1980). This superstructure was determined at 5 K from visually estimated intensities derived from a neutron powder-diffraction experiment.

The structure of anhydrous pinacol is therefore exceptional for a molecular crystal in having molecules on the sites of three different symmetries.

A few other generalizations emerged from the search. Structures with $Z' = 2$ and three molecular sites (two of which are the same) are most common in the group $C2/c$ (#15; sites 1 and either 2 or $\bar{1}$). Other more common groups are $P2_1/m$ (#11, two sites m or two sites $\bar{1}$), $P2/c$ (#13, sites 1 and either 2 or $\bar{1}$) and $Pbcn$ (#60, sites 1 and either 2 or $\bar{1}$). In almost all cases it was the sites of symmetry 2 or m that were occupied rather than the sites of symmetry $\bar{1}$.

3.2. Structures

The basic hydrogen-bonding motif, an $R_4^4(8)$ ring (Bernstein *et al.*, 1995), is the same in all the structures except the hexahydrate. The dimer motif that is common in structures of *vic*-diols (Brock, 2002) is found in the anhydrous and hexagonal phases.

3.2.1. Anhydrous pinacol. The basic packing unit (see Fig. 3) is a centrosymmetric $R_2^2(10)$ dimer formed from *gauche* molecules; the dimer is flanked by two $R_4^4(8)$ rings. Alternation in *vic*-diols of $R_2^2(10)$ and $R_4^4(8)$ rings is common (Brock, 2002); the result is a hydrogen-bonded ribbon such as is found in the hexagonal phase. In anhydrous pinacol, however, the two molecules that complete the $R_4^4(8)$ rings are not hydrogen bonded to each other. One of the two molecules lies on an inversion center and has an *anti* conformation; the other molecule lies on a twofold axis and has a *gauche* conformation.

The anhydrous structure is the only one of the structures for which the H-atom positions are well known. The hydroxyl H atoms lie slightly outside the $R_4^4(8)$ ring; the O—H···O angle is 156 (2)° at atoms H1 and H3, 169 (2)° at H2, and 166 (2)° at H4 (where H*n* is bonded to O*n*).

The six-molecule units are linked together to form sheets at $y = \frac{1}{4}$ and $\frac{3}{4}$. These sheets are somewhat corrugated, especially in the **c** direction.

3.2.2. Pinacol monohydrate. $R_4^4(8)$ rings are also present in the monohydrate structure, but the rings include two water molecules. Since $Z' = 2$, there are two separate hydrogen-bonded rings, one on inversion centers (*e.g.* at 0, $\frac{1}{2}$, $\frac{1}{2}$) and the other on twofold axes (*e.g.* at $\frac{1}{4}$, y, $\frac{1}{4}$; see Fig. 4). The average O···O distance within the rings [2.731 (18) Å] is not significantly different from the average O···O distance for the anhydrous phase at the same temperature [2.777 (6) Å].

The spreads of the O···O distances within the two kinds of rings are quite different. In the rings with $\bar{1}$ symmetry (pinacol molecule 1 that includes C1), the average distance is 2.739 (±0.002) Å, while in the rings with twofold symmetry (molecule 2 that includes C4) the average distance is 2.773 (±0.007) Å. The averages for the two rings are similar, but the difference between the two contributing values is much larger in the ring with symmetry 2.

Each pinacol molecule is part of two $R_4^4(8)$ rings. The resulting chains of rings run along **b** for molecule 1 and along **a** + **c** for molecule 2. The $R_4^4(8)$ rings are linked along **a**–**c** through water molecules (see Fig. 4).

3.2.3. Hexagonal phase. The alternating $R_2^2(10)$ and $R_4^4(8)$ rings result in the dimer ribbon pattern of O—H···O bonds (see Fig. 5) that is common among *vic*-diols (Brock, 2002). Most dimer ribbons, however, include inversion centers so that the ribbon is flat, but in this structure the twofold axes relate the two molecules of the dimer and the ribbon forms a helix around a 6_1 (or 6_5) axis. These twofold symmetry axes, which pass both through and between the dimers, guarantee that the hydroxyl H atoms are disordered. The hydroxyl H atoms in individual helices, however, are almost certainly ordered, but there is unlikely to be any correlation between the hydroxyl H-atom positions of adjacent helices.

The range of O···O distances (see Table 3) suggests strain in the helices; the distances increase with distance of the O—H···O bond from the central screw axis. The O1···O1$^{\rm i}$ [(i) $1 - y$, $1 - x$, $\frac{13}{6} - z$] distance, which is farthest away from the screw axis, is 0.131 (8) Å longer than the O2···O2$^{\rm ii}$ [(ii) $1 - x + y, y, \frac{3}{2} - z$] distance and is 0.061 (10) Å longer than the average of all the O···O distances determined in this study.

The other surprising feature of this structure is the looseness of the packing (see displacement ellipsoids in Fig. 2 and channels in Fig. 5). The ratio of observed to predicted cell volume (see above) is large. The atomic displacement ellipsoids for the C and O atoms of the pinacol molecule are large, especially for a structure determined at 173 K.

3.2.4. Pinacol hexahydrate. The hexahydrate, which was described carefully by Kim & Jeffrey (1970), has water layers composed of pentagons at $z = \frac{1}{4}$ and $\frac{3}{4}$; the layers are bridged by pinacol molecules at $z = 0$ and $\frac{1}{2}$. Since each hydroxyl group in a pinacol molecule donates a proton to a water molecule in one layer and receives a proton from a water in another layer, there are equal numbers of proton donors and acceptors in the structure. The H atoms of the water molecules and hydroxyl groups, however, must be disordered in either of the space groups $P4_2/mnm$ or $Pnnm$.

Schwarzenbach (1968) considered in detail the H-atom positions for the very similar structure of piperazine hexahydrate, which crystallizes in $P2_1/n$, but is twinned so as to appear tetragonal (space group $P4_2/mnm$). Schwarzenbach showed that the H atom could be ordered in ten different ways if the water layer included one set of 2_1 axes and no other symmetry except pure translations. It is possible to think of the pinacol hexahydrate as being ordered and twinned in a similar way, but the very obvious diffuse scattering suggests the correlation length between neighboring pinacol molecules is shorter than in a twinned crystal.

The displacement ellipsoids of the water molecules (see Fig. 2) are larger than might be expected. It is likely that there are subtle atomic displacements of the water molecules associated with the two different pinacol positions and the ten different sets of positions for the water and hydroxyl H atoms.

4. Discussion

Why does a simple molecule like pinacol produce a series of structures that are so unusual and so crystallographically perverse? Most molecules, and especially those that can conform to inversion symmetry, have simple structures with $Z' \leq 1$. The answer seems to be that the pinacol molecule is small, that it has only one important intramolecular degree of freedom and that it should participate in four O—H···O bonds.

Since the van der Waals surfaces of methyl groups are roughly spherical (albeit with a few bumps), and since conformations that have torsion angles other than *ca* 60° are unfavorable, the overall shape of pinacol is more or less fixed. The molecular shape cannot adjust much to improve the packing density.

This relatively rigid molecule should form dense crystals in which each of the two hydroxyl groups participates in two hydrogen bonds that have favorable O—H and H···O distances and C—O—H and O—H···O angles. Perhaps it is surprising that such a crystal exists. It is not surprising that co-crystals with water are formed. The hydrogen-bonding requirements of water and pinacol are very similar (two donors; two acceptors), but water is less sterically demanding.

None of these structures is especially densely packed. At 90 K the ratios $V_{\rm obx}/V_{\rm pred}$ for the $C2/c$ anhydrous, the $I2/a$ monohydrate and the $Pnnm$ hexahydrate structures are 1.016, 1.037 and 1.025 if the room-temperature volumes of Hofmann (2002) are used, and 1.004, 1.030 and 1.033 for the volumes of Mighell *et al.* (1987). The corresponding ratios for the hexagonal phase are even higher. Since volumes contract about 1% per 100 K (see *e.g.* Hofmann, 2002) ratios below 0.98 would be more normal for structures determined at 90 K. It is impossible, however, to separate the effect of significant hydrogen bonding, which holds molecules apart, from the effect of the inefficient filling of space.

4.1. Anhydrous phase

The complexity of the anhydrous pinacol structure suggests that the packing is not especially favorable because surveys of many structures show that the size of the asymmetric unit is usually minimized (Brock & Dunitz, 1994). Furthermore, structures containing more than one conformer are rare, although less rare for diols (Brock, 2002). We have found that if $Z' > 1$ there is usually an identifiable reason that can be traced to a packing problem (Koutentis *et al.*, 2001; Duncan *et al.*, 2002, Lehmler *et al.*, 2002, 2004; Hao, Chen, *et al.*, 2005; Hao, Siegler *et al.*, 2005), especially if the crystal has not been cooled for data collection. (Transitions with cooling to phases with larger unit cells are not uncommon.) In the case of pinacol the packing problem is the conflict between needing to fill space densely and needing to satisfy the hydrogen-bond donors and acceptors. This conflict is compounded by the relative inflexibility of the molecule and perhaps also by the molecule's large surface-to-volume ratio.

The disorder seen by Jeffrey & Robbins (1978) in the anhydrous pinacol structure suggests loose packing. That disorder, which is limited to the *anti* conformer, is reminiscent of the disorder found in the hexahydrate structure. If the disorder is a symptom of loose packing and if there is a low-energy pathway linking the two sites, then the structure might be expected to order as the cell contracts. Indeed at 173 K, where the packing is denser by 3.1% than at room temperature, the structure is fully ordered.

4.2. Monohydrate

The melting points (Pushin & Glagoleva, 1922) of the monoclinic monohydrate (314.4 K) and of anhydrous pinacol (314.2 K) are essentially the same, but a comparison of the temperatures is problematic because the two phases melt to give different liquids. What is certain is that no anhydrous pinacol crystal can be obtained from solutions having $X_{\rm pinacol} < 0.80$ (Pushin & Glagoleva, 1922; see Fig. 1). Comparisons of predicted volumes (see above) suggest that the monohydrate phase is less tightly packed than the anhydrous phase. The energy released by hydrogen-bond formation must compensate for the decrease in packing efficiency.

4.3. Hexahydrate

The existence of the hexahydrate, with a melting point 4.4 K above that of the anhydrous phase (Pushin & Glagoleva, 1922), is another indication that the anhydrous phase of pinacol (as well as the pure phase of water) does not have a very favorable structure, especially since the extensive disorder of the pinacol molecule in the hexahydrate is again an indication of loose packing. Clathrates such as this hexahydrate have been discussed by Jeffrey (1997).

The origin of the diffuse scattering is being investigated.

4.4. Hexagonal phase

This phase, although difficult to produce and frustrating to study, has an unremarkable pattern of O—H···O bonds. The dimer ribbons, with their alternating $R_2^2(10)$ and $R_4^4(8)$ rings, are characteristic of *vic*-diols (Brock, 2002). It is easy to imagine fragments of these ribbons existing in solution. One surprise is the twisting of the ribbons around 6_1 and 6_5 axes, because a packing pattern in which the ribbons are approximately planar would have been expected (Brock, 2002). The density of the resulting structure is very low. The fineness of the needle-like crystals indicates that growth perpendicular to the hexagonal axis is slow relative to growth along the axis. The location within a hydrophobic channel of a linear chain of water molecules, each of which probably has an unsatisfied donor and an unsatisfied acceptor, cannot be very favorable. The existence of this unsatisfactory structure again suggests that pinacol has difficulty finding a favorable crystal packing arrangement.

4.5. Related molecule

The disilyl analog of pinacol, 1,2-dihydroxytetramethyldisilane, also has a very unusual structure (Prasse *et al.*, 1999; refcode HOQTUC). The space group is *Pccn* with $Z' = 2 = 4(\frac{1}{2})$; each of the four independent molecules lies on a twofold axis. Two of the molecules are *gauche*; two are *anti*. Two hydroxyl groups from each of two molecules, and one hydroxyl group from each of four other molecules (two independent) form hydrogen-bonded cages; these cages are linked together in two directions by molecules that participate in two cages. The important difference between pinacol and the disilyl analog is the length of the central bond, which increases from 1.56 to 2.35 Å when C—C is changed to Si—Si. The longer central bond allows the formation of the unusual cages, but does not seem to permit a simple or tightly packed structure.

4.6. Might space-group frequencies vary with molecular size?

It is possible that space-group frequencies for very small molecules are somewhat different than those for larger molecules. A simple search was made of the CSD for structures containing a single molecule composed of no more than ten non-H atoms. The structures were required to have atom coordinates and an *R* factor less than 0.10. Polymeric structures and entries flagged with errors were not included. Duplicate entries (same refcode and space-group number; similar reduced cells) were removed by inspection to leave 591 hits. While 82% of the CSD structures considered by Brock & Dunitz (1994) are in the space groups $P\overline{1}$, $P2_1$, $P2_1/c$, $C2/c$ and $P2_12_12_1$, only 70% of the structures with 10 or fewer non-H atoms are in these groups. Of these very small molecules 25% crystallize in space groups with numbers (Hahn, 1983) above 19 ($P2_12_12_1$), while only 14% of all structures considered by Brock & Dunitz (1994) do. If slightly larger molecules ($\leq$ 12 non-H atoms) are considered then the corresponding frequencies (74 and 12% for 1268 hits) are more similar to those of the CSD as a whole.

Space-group frequencies for monoalcohols C_nH_mOH (Brock & Duncan, 1994) and *vic*-diols $C_nH_m(OH)_2$ (Brock, 2002) are also known to be anomalous if a full set of O—H···O bonds is formed. The unusual frequencies result from the steric requirements for hydrogen-bond formation.

It is therefore really no surprise that a very small *vic*-diol should pack in unusual ways.

5. Conclusion

While it might seem that simple molecules should be expected to have simple crystal structures, molecules that are small and simple, especially those that should participate in hydrogen bonds, may in fact be likely to give unusual and relatively complicated structures. The origin of the complexity may be the difficulty in filling space densely while also satisfying donors and acceptors when the molecule has few internal degrees of freedom.

We thank Dr James Chisholm of the Cambridge Crystallographic Data Centre for help with the searches (see Infantes *et al.*, 2003) for structures containing hydrogen-bonded chains of water molecules. We thank Richard Welberry of the Australian National University for discussions about the diffuse scattering in pinacol hexahydrate. We appreciate help from Dr Lee Brammer in obtaining a copy of the O'Connor thesis.

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