Journal of
Synchrotron
Radiation

ISSN 0909-0495

Received 2 March 2005
Accepted 5 July 2005

High-pressure polymorphism of cyclopentanol ($C_5H_{10}O$): the structure of cyclopentanol phase-V at 1.5 GPa

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The fully ordered high-pressure crystal structure of cyclopentanol ($C_5H_{10}O$) has been solved using single-crystal X-ray diffraction techniques on station 9.8 at the SRS Daresbury Laboratory. At pressures above 1.5 GPa, cyclopentanol crystallizes in the monoclinic $P2_1/c$ space group with a = 17.882 (3), b = 5.4573 (3), c = 9.6817 (14) Å, β = 104.699 (8)° and Z' = 2. The crystal structure is characterized by the formation of hydrogen-bonded molecular chains, denoted $C_2^2(4)$ in graph set notation, which lie parallel to the crystallographic c-axis, with the molecules adopting a pseudo fourfold arrangement around the central core of hydrogen bonds.

Keywords: high pressure; single-crystal diffraction; small-molecule.

1. Introduction

Molecular materials contain a rich spectrum of interaction types – from the relatively weak van der Waals interaction, through the more moderate ionic bond and hydrogen bond, to the relatively strong covalent bond – and as these interactions depend strongly on intermolecular distance, high pressure provides a powerful means of altering their relative hierarchy of strengths. A systematic study of molecular systems at high pressure is rewarding, therefore, as competition between the various interaction types causes phase transitions, including glass formation, and effects melting, crystal solubility and nucleation. Despite the rich high-pressure behaviour we expect to be exhibited by molecular systems at high pressure, until comparatively recently the majority of research in high-pressure structural science has focused on the study of fundamental systems such as the elements and simple compounds, for example alloys, semiconductors and minerals, some of which can exhibit a surprisingly complex structural behaviour (for example, Nelmes *et al.*, 1999). With the exception of molecules of relevance to planetary science (such as ice, methane and ammonia) there has been relatively little work conducted on simple generic molecular systems containing common functional groups such as the mono-alcohols, monocarboxylic acids, ketones and nitriles, nitro compounds, amines *etc.*, despite their fundamental importance to the understanding of whole classes of compounds.

Over the past few years, along with only a very small number of other groups world-wide, we have been conducting a systematic series of studies on the high-pressure crystal structures of a variety of molecular systems including organic materials, such as simple functional compounds (Allan *et al.*, 1998, 1999, 2000, 2002*a*; Allan & Clark, 1999*a*,*b*, 2000), pharmaceutical compounds (Fabbiani *et al.*, 2003, 2004), amino acids (Moggach *et al.*, 2005), peptides and, more recently, proteins, along with inorganic materials, such as the oxoacids and their hydrates (Allan *et al.*, 2002*b*). All of these systems have been studied, principally, with single-crystal X-ray diffraction techniques and, as many of the compounds are liquids at ambient conditions, the crystals have often required to be grown within the diamond-anvil cell once the compound has been 'frozen' on the application of pressure. It is more usual, though, for single crystals to be grown *ex situ*, from solution for example, and then cut to the correct size before they are loaded into the gasket of the diamond-anvil cell. On pressure increase, however, any subsequent structural phase transition could shatter the crystal or the kinetic barrier may be sufficiently large for such a transition that the crystal remains kinetically trapped in a metastable structure. The growth of single crystals *in situ* from the melt, although it can often prove to be extremely problematic, overcomes both of these fundamental difficulties and the high-pressure equilibrium phase can be obtained. For compounds that have a relatively high melting point, decomposition can often occur before the onset of melting and this effect is exacerbated by pressure as this can raise the melting point still further. However, we have recently adopted solvothermal methods for the crystal growth of compounds at high pressure and this largely overcomes the problem of decomposition (Fabbiani *et al.*, 2004). In this method, the diamond-anvil cell is loaded with a saturated solution of the compound and pressure is used to precipitate crystals. There is no need to apply large tempera-

tures to grow a single crystal as the lattice energy is largely overcome by the energy of solvation and this allows us to study a wider range of compounds in a variety of different solvents. We have already applied this methodology with great success on a number of pharmaceutical compounds.

Apart from developing methods for the preparation of single crystals at high pressure, we have also developed new single-crystal X-ray diffraction techniques for the new generation of diffractometers equipped with CCD area detectors (Dawson *et al.*, 2004). These new methods, which were originally developed for conventional X-ray tube sources at our home laboratory, have been crucial to the subsequent success of our high-pressure single-crystal X-ray diffraction studies on station 9.8 at the SRS Daresbury Laboratory. Here we report an example of one of our recent studies at SRS, where we have combined the techniques of crystal growth from the melt at high pressure with single-crystal diffraction techniques using synchrotron radiation, to determine the fully ordered high-pressure structure of cyclopentanol ($C_5H_{10}O$).

There has been considerable experimental and theoretical interest in the reorientational motion of molecules in the solid state (for example, Ceccaldi, 1985; Bessada *et al.*, 1988; Tamarit *et al.*, 1997). Timmermans (1938) observed that crystals composed of approximately spherical molecules have relatively small entropy and volume discontinuities at the melt. These systems, described as plastic crystals or orientationally disordered crystals, often display at least one additional transition on cooling below the melt with an accompanying relatively large change in entropy as the disordering of the molecules 'freezes out' at the disordered-to-ordered low-temperature phase transition. This freezing can occur in steps on cooling, as indicated by further thermodynamic anomalies, with successive rotational degrees of freedom locking-in to increase the degree of ordering in the crystal.

Cyclopentanol ($C_5H_{10}O$) is a relatively simple example of a molecular material that forms plastic crystalline phases on initial cooling. Its polymorphism has been studied at both low temperature and high pressure using a variety of techniques such as calorimetry, spectroscopy, high-pressure density measurements, NMR spectroscopy and X-ray powder diffraction (Rute *et al.*, 2003). The X-ray powder diffraction studies indicate that cyclopentanol forms two plastic crystalline phases below its melting point of 255 K. The first of these plastic phases, phase-I [a = 5.883 (1), c = 9.479 (2) Å, Z = 2 at 243.2 K], crystallizes in hexagonal symmetry with the molecules adopting a close-packed arrangement in which each molecule rotates about its centre of mass which imposes spherical symmetry. On cooling below 236 K, the second orientationally disordered phase of cyclopentanol is formed, phase-II [a = 10.0996 (14), c = 9.500 (2) Å and Z = 6 at 217.2 K]. In the crystal structure of phase-II, the molecules retain the same positions as they adopt in the lattice of phase-I, but complete rotational freedom is lost so that the rotation of the molecules is restricted about some fixed axis. On further cooling, rotational freedom of the molecules is lost completely and two fully ordered phases are formed. The first of these ordered phases, phase-III, is found to be stable below a temperature of 202 K and its X-ray powder diffraction pattern was indexed on a relatively large unit cell with either *Cc* or *C*2/*c* monoclinic symmetry, a = 23.949 (3), b = 6.3178 (7), c = 21.829 (2) Å, β = 100.16 (1)° at 199 K with 24 molecules per unit cell. At a temperature of 176 K, a phase transition to a second monoclinic structure, phase-IV, was identified from discontinuities in the temperature dependence of the lattice parameters, principally in b and β. The subtle nature of the transition suggests that it is second order in character and, given the effects of thermal expansion, powder patterns obtained from phase-IV can be indexed on essentially the same unit cell as that of phase-III: for phase-IV at 123 K, a = 23.598 (6), b = 6.2801 (7), c = 21.405 (2) Å, β = 100.32 (1)°. Despite the apparently successful indexing of the powder patterns obtained using laboratory-based techniques on a sealed-tube source, the crystal structures of these ordered phases could not be determined (Rute *et al.*, 2003).

Here we report a high-pressure structural study of cyclopentanol where we have used single-crystal X-ray diffraction techniques to solve the structure of a previously unobserved and fully ordered phase. This work is part of our on-going studies into the low-temperature and high-pressure structural behaviour of simple molecular materials. We have already studied the high-pressure polymorphism of a number of small-molecule systems including alcohols, di-alcohols, ketones, amino acids and simple peptides and, more recently, we have been investigating both the low-temperature and high-pressure behaviour of cyclic molecules, such as cyclopropylamine and cyclobutanol. For cyclobutanol we find that the crystal structures of both the low-temperature and high-pressure phases are fully ordered and are characterized by the formation of hydrogen-bonded molecular chains. In the low-temperature structure, these chains form an approximate threefold molecular arrangement with a hydrogen-bonded central core while, in contrast, the chains of the high-pressure phase adopt a quite different wave-like topological arrangement (McGregor *et al.*, 2005).

With the initial success of the high-pressure and low-temperature single-crystal X-ray diffraction studies of the high-pressure structural behaviour of cyclobutanol, we have extended our work on cyclic alcohols to include studies on the high-pressure structural behaviour of cyclopentanol. On initial compression to a relatively modest pressure of 0.7 GPa, cyclopentanol crystallizes in the fully rotationally disordered phase-I structure, but on subsequent compression to 1.5 GPa, and recrystallization from the melt, a previously unobserved and fully ordered crystalline phase is found to be stable. As the structure is reasonably complex and the diffracted intensity concomitantly weak, the most strongly diffracting reflections were found to be only barely measurable on our laboratory-based sealed-tube source. Consequently, the full structural characterization was conducted using synchrotron radiation on station 9.8 at SRS Daresbury Laboratory. As for both the low-temperature and high-pressure structures of cyclobutanol, the crystal structure of this new phase, phase-V, of cyclopentanol is also characterized by the formation of

hydrogen-bonded molecular chains, although here they adopt an approximate fourfold arrangement.

2. Experiment and data analysis

The sample was prepared by loading cyclopentanol (of 99% purity, as received from Aldrich) into a Merrill–Bassett diamond-anvil cell (Merrill & Bassett, 1974) that had been equipped with 600 μm culet diamonds and a tungsten gasket. The sample was pressurized at room temperature until the crystallization of several crystallites was observed. The temperature was then increased, so that the polycrystalline sample was partially remelted, and subsequently cycled close to this elevated melting temperature in order to reduce the number of crystallites. This process proved to be difficult as the crystallites displayed no obvious growth habits and the appearance of the sample was not affected by crossed polarisers. A single crystal was eventually obtained at a pressure of 0.7 GPa, measured using the ruby fluorescence technique, which could be indexed on an Enraf–Nonius CAD4 four-circle diffractometer (graphite monochromated Mo $K\alpha$ radiation) on essentially the same unit cell as that of phase-I of cyclopentanol, albeit with a 12% reduction in the unit-cell volume [hexagonal, a = 5.618 (5), c = 9.116 (2) Å and V = 249.2 (5) Å^3]. Only a very limited number of relatively strong reflections could be observed at low diffraction angles, which is indicative of the complete rotational disorder of the molecules in this phase. The sample pressure was subsequently increased and the crystal growth procedure repeated. Although the melting temperature of the sample was substantially higher, observation of the crystallites proved rather less problematic than before as individual crystallites could now be observed with a cross-polarizing microscope. Nevertheless, the growth of a good quality single crystal proved extremely difficult and several attempts were required before a sample suitable for structure solution could be obtained. Initial X-ray diffraction studies at our home laboratory indicated that a new phase was stable above approximately 1.5 GPa, but the diffraction data were too weak for full structure determination and only the rather tentative identification of a monoclinic unit cell was possible. In order to solve the structure of this high-pressure phase, we conducted a single-crystal X-ray diffraction study using synchrotron radiation.

X-ray diffraction data (λ = 0.6777 Å) were collected on a Bruker APEX CCD diffractometer on station 9.8 at CCLRC SRS Daresbury Laboratory. Data were collected in ω-scans in 16 settings of 2θ and φ, see Table 1; this strategy is a slight modification of that described by Dawson *et al.* (2004). The data were integrated using the program *SAINT* (Siemens, 1995) using 'dynamic masks' to avoid integration of regions of the detector shaded by the body of the pressure cell (Dawson *et al.*, 2004). Absorption corrections were carried out using the programs *SADABS* (Sheldrick, 2001) and *SHADE* (Parsons, 2004), while merging was carried out in *SORTAV* (Blessing, 1997) with robust-resistant weights.

Table 1
High-pressure data-collection selection sequence for the Bruker APEX CCD diffractometer.

This strategy is a modification of that outlined by Dawson *et al.* (2004).

Run	2θ (°)	φ (°)	Range of ω (°)
1	27	180	30.00 to 0
2	10	180	0.00 to −20
3	0	180	−20.00 to −30
4	0	180	−150.00 to −160
5	−10	180	−160.00 to −180
6	−27	180	−180.00 to −210
7	−27	180	−5.00 to −30
8	27	180	−150.00 to −175
9	27	360	30.00 to 0
10	10	360	0.00 to −20
11	0	360	−20.00 to −30
12	0	360	−150.00 to −160
13	−10	360	−160.00 to −180
14	−27	360	−180.00 to −210
15	−27	360	−5.00 to −30
16	27	360	−150.00 to −175

Determinations of the cell parameters of the sample showed that an ordered new phase of cyclopentanol had been grown at 1.5 GPa. The crystal was monoclinic, and its unit-cell dimensions were a = 17.882 (3), b = 5.4573 (3), c = 9.6817 (14) Å and β = 104.699 (8)° based on 942 data, $8 < 2\theta < 45°$, with $Z' = 2$. The structure of the new phase was solved by direct methods, in $P2_1/c$ space-group symmetry using the program *SIR92* (Altomare *et al.*, 1994).

Refinements were carried out against $|F|^2$ using all data (*CRYSTALS*; Betteridge *et al.*, 2003). Because of the low completeness of the data sets (40.1%), all C—C and C—O bond distances were restrained to values obtained from *International Tables for Crystallography*, Volume C, for organic sp^3—sp^3 and sp^3—O (alcohol) bonds (Allen *et al.*, 1987), respectively. Standard uncertainties for these bonds within *International Tables* were also those used for the restraints. All C and O atoms were refined with anisotropic displacement parameters. H atoms attached to carbon were placed geometrically and not refined, whilst those on the O atoms were found in a difference map, restrained and refined. Crystal structures were visualized using the programs *CAMERON* (Watkin *et al.*, 1993) and *MERCURY* (Bruno *et al.*, 2002). Analyses were carried out using *PLATON* (Spek, 2004), as incorporated in the *WIN-GX* suite (Farrugia, 1999). Details of the crystal, data collection and refinement statistics are given in Table 2, while the refined crystallographic structural and thermal displacement parameters are listed in Tables 3 and 4. The asymmetric unit, including details of the atomic numbering scheme, is illustrated in Fig. 1.

3. Results and discussion

3.1. Intramolecular geometry

Although the intermolecular geometry and hydrogen bonding present in the ordered high-pressure phase-V structure of cyclopentanol will be discussed, the intramolecular geometry is also worthy of discussion as the conformation of

Table 2
Experimental details for the high-pressure structure determination of cyclopentanol at 1.5 GPa.

Crystal data	
Chemical formula	C_5H_9OH
Chemical formula weight	86.13
Cell setting, space group	Monoclinic, $P2_1/c$
a, b, c (Å)	17.822 (3), 5.4573 (3), 9.6817 (14)
β (°)	104.699 (8)
V (Å^3)	913.92 (19)
Z	8
D_{calc} (Mg m^{-3})	1.252
Radiation type	Synchrotron, 0.6777 Å
No. of reflections for cell parameters	942 ($8^\circ < \theta < 45^\circ$)
μ (mm^{-1})	0.084
Crystal form, colour	Cylindrical, colourless
Radius (mm)	0.1
Thickness (mm)	0.08
Temperature (K)	293 (2)
Data collection	
Diffractometer	CCD area detector
Data collection method	ω scans
Absorption correction	Semi-empirical from equivalents
T_{min}	0.63
T_{max}	0.98
No. of measured, independent and observed parameters	3739, 592, 418
Criterion for observed reflections	$I > 4\sigma(I)$
R_{int}	0.082
Θ_{max} (°)	23.29
Range of h, k, l	$-14 \rightarrow h \rightarrow 14$ $-6 \rightarrow k \rightarrow 6$ $-9 \rightarrow l \rightarrow 9$
Refinement	
Refinement on	F^2
$R[F^2 > 4\sigma(F^2)]$, $wR(F^2)$, S	0.0487, 0.1278, 0.9318
No. of reflections and parameters used in refinement	542, 115
H-atom treatment	Riding, hydroxyl H atoms refined
Weighting scheme	$W = 1/\sigma^2(F_o^2) + (0.054P)^2 + (1.163P)$, $P = 1/3\ \max(F_o^2, 0) + (2/3F_c^2)$
$(\Delta/\sigma)_{max}$	0.000034
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.17, −0.18
No. of restraints	107

Table 3
Atomic fractional coordinates and equivalent isotropic displacement parameters (Å^2 × 10^3) for the high-pressure crystal structure of cyclopentanol at 1.5 GPa.

U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C1	0.0826 (3)	−0.1257 (6)	0.3901 (5)	27
H11	0.0812	−0.2942	0.4299	34
H12	0.0431	−0.0207	0.4185	34
C2	0.0685 (4)	−0.1340 (6)	0.2287 (5)	30
H21	0.0887	−0.2904	0.1983	35
H22	0.0120	−0.1196	0.1818	35
C3	0.1127 (4)	0.0870 (6)	0.1901 (5)	25
H31	0.1464	0.0338	0.1275	32
H32	0.0756	0.2145	0.1396	32
C4	0.1621 (4)	0.1885 (6)	0.3310 (5)	33
H41	0.2159	0.2229	0.3235	39
H42	0.1388	0.3422	0.3579	39
C5	0.1623 (3)	−0.0151 (6)	0.4412 (5)	26
H51	0.1712	0.0526	0.5401	32
O6	0.2204 (3)	−0.1925 (4)	0.4313 (4)	33
H61	0.2460 (40)	−0.2360 (60)	0.5210 (30)	40
C11	0.3381 (5)	0.1631 (7)	0.1462 (7)	44
H111	0.3606	0.3199	0.1920	52
H112	0.2824	0.1885	0.0969	52
C12	0.3831 (5)	0.0744 (7)	0.0383 (6)	36
H121	0.4207	0.2023	0.0251	42
H122	0.3466	0.0362	−0.0559	42
C13	0.4258 (4)	−0.01576 (6)	0.1046 (6)	34
H131	0.4803	−0.1563	0.0953	41
H132	0.3987	−0.3072	0.0570	41
C14	0.4248 (4)	−0.01520 (6)	0.2588 (6)	32
H141	0.4680	−0.0488	0.3154	37
H142	0.4290	−0.3213	0.2995	37
C15	0.3467 (4)	−0.0390 (6)	0.2582 (6)	32
H151	0.3464	0.0291	0.3539	37
O16	0.2872 (3)	−0.2201 (6)	0.2118 (4)	40
H161	0.2580 (30)	−0.2490 (100)	0.2740 (50)	48

Table 4
Anisotropic displacement parameters (Å^2 × 10^3) for the non-H atoms in the high-pressure structure of cyclopentanol, at 1.5 GPa.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	31 (4)	25 (2)	29 (3)	5 (2)	17 (3)	1 (2)
C2	35 (6)	24 (2)	27 (3)	4 (2)	5 (4)	−5 (2)
C3	24 (6)	31 (2)	25 (3)	8 (2)	15 (4)	4 (2)
C4	37 (6)	18 (2)	43 (4)	2 (2)	8 (4)	−5 (2)
C5	30 (4)	24 (2)	25 (3)	−2 (2)	6 (4)	6 (2)
C11	58 (6)	25 (2)	46 (4)	4 (2)	11 (4)	10 (2)
C12	42 (6)	27 (2)	36 (4)	5 (2)	3 (4)	−1 (2)
C13	38 (6)	28 (2)	37 (3)	4 (2)	8 (4)	0 (2)
C14	33 (4)	26 (2)	33 (3)	3 (2)	0 (4)	−4 (2)
C15	38 (5)	23 (2)	31 (3)	−6 (2)	3 (3)	−3 (2)
O6	34 (4)	41 (2)	26 (3)	3 (1)	11 (3)	15 (2)
O16	36 (5)	43 (2)	40 (4)	−11 (2)	8 (4)	−12 (2)

the molecule must almost certainly contribute to the stabilization of a preferred structure at high pressure. The conformation of cyclic alcohols is dependent on the geometry of the ring with a finite number of puckered conformations available. Cyclopentanol can display two such conformations: the envelope and half-chair. The position of the hydroxyl group, which itself can adopt two positions, the axial and equatorial, also has to be taken into account. Although steric effects will in no doubt be a major contributor to the possible packing of an ordered structure, the conformation of the polar hydroxyl group is vital for the stabilization of an ordered structure owing to its hydrogen-bonding ability.

The high-pressure phase-V structure of cyclopentanol ($Z' = 2$) has both symmetry-independent molecules in the half-chair conformation with the hydroxyl groups in both molecules adopting the axial position. The half-chair conformation is supported by the calculated puckering parameters (Cremer & Pople, 1975), while conformational analysis (Evans & Boeyens, 1989), Table 5, of both cyclopentanol molecules clearly shows that, although both five-membered rings within the cyclopentanol molecules demonstrate the half-chair conformation, both show distortion towards the envelope form with the C11 to C15 ring showing greatest distortion toward this form. The difference between conformations of both molecules is also represented graphically in Fig. 2 in which both symmetry-independent molecules are shown

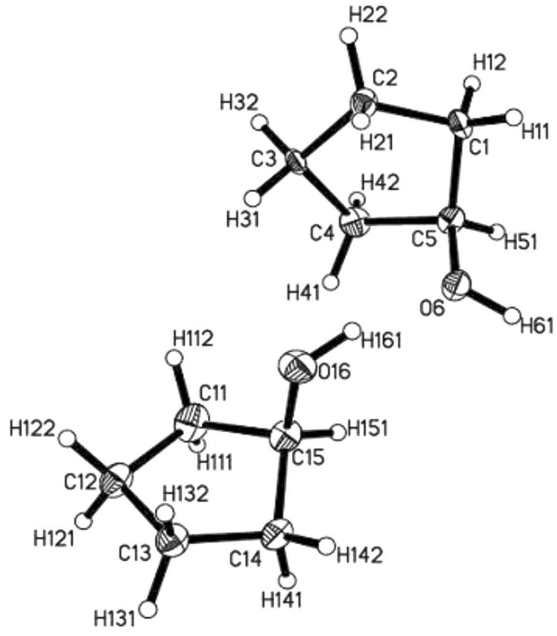

Figure 1
The asymmetric unit, and atomic numbering scheme, for the high-pressure crystal structure of cyclopentanol at 1.5 GPa. The non-H atoms are shown with displacement ellipsoids to a probability level of 30%.

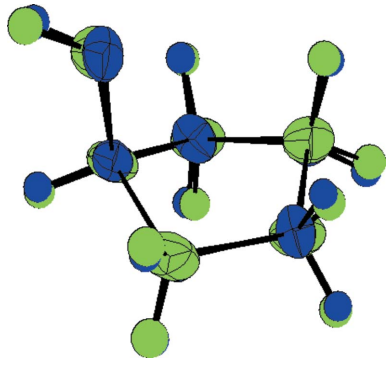

Figure 2
The different colours represent the two symmetry-independent molecules in cyclopentanol phase-V. Both are shown overlapped, fitted to the best plane of the molecule using the program *CAMERON* (Watkin *et al.*, 1993).

overlapped [fitted to the best plane of the molecule using *CAMERON* (Watkin *et al.*, 1993)]. In both of the molecules, the hydroxyl groups are oriented so that they adopt an eclipsed conformation with respect to the C—H bond of the C atoms to which they are attached.

3.2. Hydrogen-bonding motif and molecular packing

The general features of the packing motifs adopted by mono-alcohols and mono-phenols, *R*OH, have been described by Brock & Duncan (1994), and also Taylor & Macrae (2001), where there is a competition between the packing requirements of the relatively bulky *R*-group and the demand for the small hydroxyl groups to come within sufficient proximity for hydrogen bonding to occur. If the molecules containing the hydroxyl groups are relatively 'thin' (by Brock's terminology)

Table 5
Cremer and Pople puckering parameters Q_2 and φ_2, and primitive coefficients for Evans and Boeyens conformational analysis of five-membered rings in both symmetry-independent cyclopentanol phase-V molecules, both demonstrating distortion towards the envelope form, with C11 to C15 showing greatest distortion toward this form.

Ring	Q_2	φ_2	cos form	sin form
C1 to C5	0.3906 (54)	337.8 (8)	0.093	0.301
C11 to C15	0.3845 (65)	299.9 (10)	0.132	0.257

then they can be related by a glide plane or a 2_1 screw axis so that the molecules form an approximately coplanar alternating sequence about the central hydrogen-bonded core. For bulkier *R*-groups, steric hindrance often prohibits the molecules adopting this simple arrangement and, instead, these systems often form chains about three-, four- or sixfold screw axes, or adopt crystal structures with more than one molecule in the asymmetric unit. If the *R*-group is particularly bulky then the molecules may no longer form hydrogen-bonded chains, or catemers, but cyclic dimer, trimer, tetramer or hexamer rings can be created.

In our recent high-pressure structural studies of phenol (Allan *et al.*, 2002*a*,*b*) and its halogenated derivatives 2-chlorophenol and 4-fluorophenol (Oswald *et al.*, 2005*a*,*b*), we have observed a clear change in the nature of the *R*-group packing behaviour. All three systems form crystal structures at ambient pressure characterized by the formation of hydrogen-bonding schemes associated with bulky *R*-groups. Both phenol (space group $P2_1$, $Z' = 3$) and 2-chlorophenol (space group $P3_2$, $Z' = 1$) form crystal structures where the molecules are hydrogen bonded into threefold helical chains. For phenol, the arrangement of the three molecules that compose the repeat unit of the pseudo threefold helix are not related to one another by symmetry, and the 2_1 screw axis only relates neighbouring hydrogen-bonded molecular chains, while for 2-chlorophenol the hydrogen-bonded chains are strictly threefold in character with the molecules arranged about crystallographic 3_2 screw axes. The ambient-pressure structure of 4-fluorphenol has a markedly different packing arrangement with the molecules hydrogen bonding to form hexamer rings about threefold rotoinversion sites. On application of pressure, however, all three systems form crystal structures with the molecules disposed along chains that are generated by 2_1 screw axes. In effect, pressure has transformed the packing behaviour of the phenyl and halophenyl groups from having characteristics more closely associated with bulky groups to those more typical of small groups, with an accompanying partial closure of the intermolecular voids.

We have also observed similar high-pressure behaviour in cyclobutanol (McGregor *et al.*, 2005) where the *R*-groups are sufficiently small, unlike the heavier cyclopentanol, to allow sterically unhindered hydrogen bonding between the hydroxyl groups. The low-temperature crystal structure (space group *Aba*2, $Z' = 2$) is fully ordered and is composed of pseudo threefold molecular chains which lie parallel to the crystallographic *a*-axis. At high pressure, the crystal space-group symmetry changes to $Pna2_1$ ($Z' = 1$) and the molecular chains,

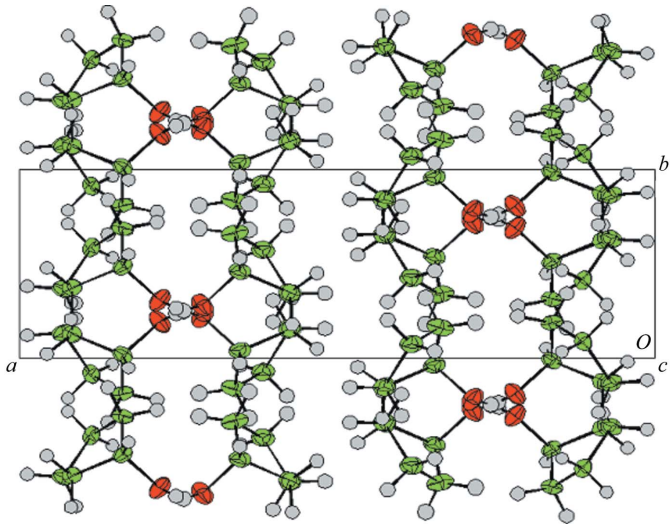

Figure 3
The high-pressure crystal structure of cyclopentanol in *c*-axis projection. The pseudo fourfold nature of hydrogen-bonded molecular chains is apparent.

which are generated by the *a*-glide symmetry, adopt a pseudo twofold arrangement.

For the current study on cyclopentanol, we find that the application of pressure has resulted in the formation of an ordered phase after the initial crystallization of the rotationally disordered hexagonal phase-I. The fully ordered monoclinic structure is characterized by the formation of hydrogen-bonded molecular chains, denoted $C_2^2(4)$ in graph set notation, which lie parallel to the crystallographic *c*-axis. The molecules adopt a pseudo fourfold arrangement around the core of hydrogen bonds (see Figs. 3 and 4). The two molecules in the asymmetric unit are hydrogen bonded together to form a single section of the chain and the *c*-glide symmetry links these sections in pairs to construct the complete catemer. Strictly, these catemers are not helical in nature, as helices are not supported by the *c*-glide symmetry, and adjacent molecules bridging the selected asymmetric unit (Fig. 1 and Table 3) have hydroxyl groups that are aligned anti-parallel with one another (as defined by the directions of the C5—O6 and C15—O16 bonds) rather than perpendicular as would be expected for an ideal fourfold helix. [The C15—O16—O6—C5 torsion angle is 84.3 (5)° within the asymmetric unit while the bridging torsion angle is 175.7 (5)°.] The hydrogen bond lengths and bond angles are shown in Table 6. This fourfold arrangement is characteristic of a bulky group in Brock and Duncan's scheme. The increase from the pseudo threefold symmetry of the low-temperature structure of cyclobutanol to the pseudo fourfold symmetry of the ordered high-pressure structure of cyclopentanol is concomitant with the increase in size, or bulk, of the *R*-group. Clearly though, the bulky characteristics of the C_5H_9 *R*-group at pressure is perhaps a little unexpected as, from the trend of behaviour that we have observed in the other mono-alcohols, we would have anticipated that the cyclopentanol molecules would have formed the pseudo twofold catemers more normally associated with small *R*-groups. However, the high-pressure structural behaviour of 3-chloro-, 3-fluoro-, 4-chloro- and 2-fluorophenol shows a departure from that observed in phenol, 2-chlorophenol and 4-fluorophenol, and is more in accord with our observations for cyclopentanol (Oswald *et al.*, 2005*b*). For these monofluoro- and monochlorophenols, the transition from a bulky alcohol packing to a small alcohol packing is not observed and it is found that they crystallize in pseudo-helices and ring motifs, although these are considerably distorted from the three- or fourfold symmetry often observed in alcohol structures. The high-pressure crystal chemistry of cyclopentanol, along with that of monohalogenated phenols, suggests that *R*-groups of this size have a structural behaviour that is on the borderline between small alcohol and bulky alcohol crystal packing. With the absence of complete structure determinations of either of the two ordered, phase-III and phase-IV, low-temperature structures of cyclopentanol, however, it is not possible to say what packing arrangement the C_5H_9 groups have in the ordered phase-III and phase-IV structures at ambient pressure. It is entirely reasonable,

Table 6
Selected hydrogen bond lengths and bond angles for the high-pressure crystal structure of cyclopentanol.

Note that the *D*—H distances were restrained (as described in the text).

	D—H (Å)	H···*A* (Å)	*D*— H···*A* (°)	*D*···*A* (Å)
O6—H61	0.901 (9)	1.825 (15)	169 (5)	2.717 (5)
O16—H161	0.901 (9)	1.844 (25)	156 (5)	2.694 (9)

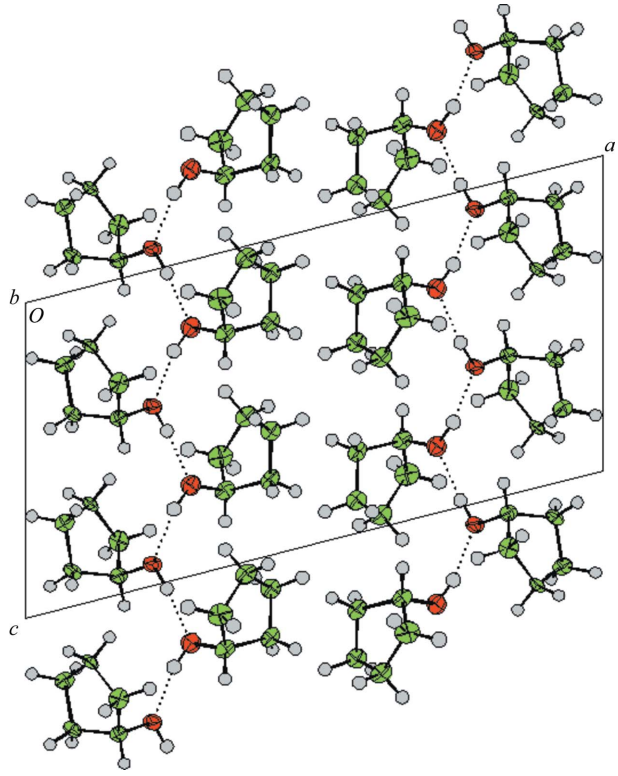

Figure 4
The high-pressure crystal structure of cyclopentanol in *b*-axis projection. The pseudo fourfold molecular catemers can be observed to run parallel to the *c*-axis in this view. The hydrogen bonds are shown as dotted lines.

however, to expect that these low-temperature phases will have more open structures and they could be characterized by the formation of either cyclic hydrogen-bonded rings of molecules, or catemers with higher-order pseudo rotational symmetry. If this were the case, then the formation of the pseudo fourfold arrangement at pressure could be considered to be consistent with the trend towards small-group behaviour. Consequently, with the structural determination of the high-pressure ordered phase the full solution of phases III and IV becomes increasingly more important.

3.3. Voronoi-Dirichlet molecular packing analysis

In our previous studies of the high-pressure structural chemistry of other small-molecule systems we have found it extremely valuable to analyse the overall molecular packing as this is indicative of the change in overall molecular contacts. Blatov and co-workers have studied the topological characteristics of packing in molecular crystals structures where they visualized the coordination environment of a molecule in a crystal structure using a Voronoi-Dirichlet polyhedron (VDP) (Peresypkina & Blatov, 2000*a*,*b*). Voronoi-Dirichlet analysis is a method for partitioning space amongst points which occupy that space. A point is separated from a neighbouring point by a plane which bisects the vector between them, in a manner analogous to the construction of a Wigner-Seitz cell for a lattice. This construction is repeated for every pair of points to yield a subdivision of the space into cells which each contain one point.

The effect of pressure on the molecular packing of the cyclopentanol molecules can be gauged by comparison of the lattice VDPs of the low-temperature plastically disordered phase-I structure with that of the fully ordered high-pressure phase-V structure. For the phase-I structure, the coordination sequence is that of ideal hexagonal close-packed, 12-44-96, where the molecular coordination number is 12 and there are 44 and 96 molecules in the second and third coordination spheres, respectively. The corresponding VDP is shown in Fig. 5(*a*). In the high-pressure phase-V crystal structure, the coordination sequence for both molecules in the asymmetric unit is 14-50-110, where the molecular coordination number is 14. Fourteen is the most commonly observed value in molecular structures, and ideally the VDP is a cuboctahedron, as observed in the body-centred cubic structure of tungsten (Fig. 5*b*). The VDPs of the two independent molecules in cyclopentanol-V are shown in Figs. 5(*c*) and 5(*d*), and they clearly correspond to distorted versions of the cuboctahedron shown in Fig. 5(*b*). It is also interesting to note that the VDPs of both of the molecules in the asymmetric unit are actually very similar, as can be seen in the figure, and this indicates that their respective environments are broadly the same.

This change in the packing behaviour is similar to what we have previously observed in the high-pressure crystal chemistry of cyclobutanol. VDP analysis of the low-temperature *Aba*2 phase and the high-pressure $Pna2_1$ phase revealed that the molecular packing of both crystal structures was similar to that found in body-centred cubic (b.c.c.). As the polyhedron for the high-pressure phase, however, was found to be less distorted from the ideal b.c.c. surface, it was concluded that the change in the crystal structure of cyclobutanol on application of pressure can be considered to be driven by the adoption of a packing arrangement which more closely resembles that adopted in hard-sphere structures. For cyclopentanol, the plastically disordered phase-I structure already adopts hexagonal close packing and, by applying pressure to form the fully ordered phase-V, it appears that this ideal packing arrangement has been disrupted. However, given that phase-V is fully ordered and contains hydrogen-bonded catemers, the change to the b.c.c. arrangement is entirely consistent with the behaviour of cyclobutanol and other hydrogen-bonded molecular systems.

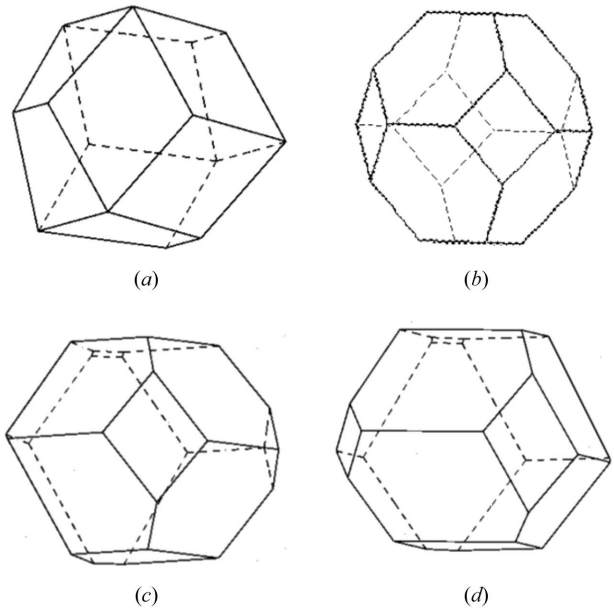

Figure 5
Lattice Voronoi-Dirichlet polyhedra. (*a*) Hexagonal close-packed structure of cyclopentanol-I. (*b*) Perfect body-centred cubic structure of tungsten at room temperature. (*c*, *d*) Components of the asymmetric unit of cyclopentanol-V at 1.5 GPa; (*c*) is the VDP for molecule 1 (C1 to C5) and (*d*) is the VDP for molecule 2 (C11 to C15).

4. Conclusions

We have solved the high-pressure, fully ordered, crystal structure of cyclopentanol. We find that on initial compression the plastically disordered hexagonal phase-I structure is stable but, at pressures above 1.5 GPa the ordered monoclinic structure, that we tentatively label phase-V, is formed. It is characterized by the formation of pseudo fourfold molecular catemers which are disposed along the crystallographic *c*-axis and are generated by the *c*-glide symmetry. This form of catemer is consistent with the relatively bulky C_5H_9 group. The trend towards the favouring of small *R*-group packing at pressure suggests that the, as yet unsolved, phase-III and phase-IV low-temperature structures may have relatively open structures composed of either cyclic hydrogen-bonded rings of molecules or catemers with high-order pseudo rota-

tional symmetry. Certainly, we expect there to be further structural phase transitions at higher pressure and these may lead towards a crystal structure containing pseudo twofold catemers, paralleling the behaviour we have already observed for cyclobutanol, phenol and its halogenated derivatives 2-chlorophenol and 4-fluorophenol. VDP analysis of the molecular packing arrangement indicates that phase-V of cyclopentanol adopts a b.c.c. arrangement. This behaviour is consistent with our previous observations of the high-pressure structural chemistry of cyclobutanol and other hydrogen-bonded systems.

The current study also illustrates that it is now possible to obtain extremely high-quality high-pressure single-crystal X-ray diffraction data sets using synchrotron radiation. Although the pressure required to produce cyclopentanol-V was fairly modest, and the sample volume could be relatively large as a consequence, the techniques highlighted here, and by Dawson *et al.* (2004) and Moggach *et al.* (2005), could be readily applied to much smaller samples for significantly higher pressure regimes.

We are indebted to Dr J. E. Warren, of Daresbury Laboratory, and Dr S. J. Teat, now of the Diamond synchrotron light source, for their continued help and support with the single-crystal diffraction facilities of station 9.8 at SRS. We also thank the Engineering and Physical Sciences Research Council of the UK for funding SAM's PhD studentship and DRA's EPSRC Advanced Research Fellowship.

References

Allan, D. R. & Clark, S. J. (1999*a*). *Phys. Rev. Lett.* **82**, 3464–3467.
Allan, D. R. & Clark, S. J. (1999*b*). *Phys. Rev. B*, **60**, 6328–6334.
Allan, D. R. & Clark, S. J. (2000). *Science and Technology of High Pressure, Proceedings of AIRAPT-17*, pp. 395–398. Hyderabad: Universities Press.
Allan, D. R., Clark, S. J., Brugmans, M. J. P., Ackland, G. J. & Vos, W. L. (1998). *Phys. Rev. B*, **58**, R11809–R11812.
Allan, D. R., Clark, S. J., Dawson, A., McGregor, P. A. & Parsons, S. (2002*a*). *Acta Cryst.* B**58**, 1018–1024.
Allan, D. R., Clark, S. J., Dawson, A., McGregor, P. A. & Parsons, S. (2002*b*). *J. Chem. Soc. Dalton Trans.* **8**, 1867–1871.
Allan, D. R., Clark, S. J., Parsons, S. & Ruf, M. (2000). *J. Phys. Condens. Matter*, **12**, L613–L618.
Allan, D. R., Ibberson, R. M., Parsons, S., Clark, S. J., Pulham, C. R. & Sawyer, L. (1999). *Chem. Commun.* p. 751.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. 1972–1999.
Altomare, A., Burla, M. C., Camalli, G., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435–436.
Bessada, C., Fuchs, A. H., Rousseau, B. & Szwarc, H. (1988). *J. Phys. C*, **21**, 731–737.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
Brock, C. P. & Duncan, L. L. (1994). *Chem. Mater.* **6**, 1307–1312.
Bruno, I. J., Cole, J. C., Edington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Ceccaldi, D. (1985). *Phys. Rev. B*, **31**, 8221–8225.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dawson, A., Allan, D. R., Parsons, S. & Ruf, M. (2004). *J. Appl. Cryst.* **37**, 410–416.
Evans, G. G. & Boeyens, J. A. (1989). *Acta Cryst.* B**45**, 581–590.
Fabbiani, F. P. A., Allan, D. R., David, W. I. F., Moggach, S. A., Parsons, S. & Pulham, C. R. (2004). *Cryst. Eng. Commun.* **6**, 504–511.
Fabbiani, F. P. A., Allan, D. R., Dawson, A., David, W. I. F., McGregor, P. A., Oswald, I. D. H., Parsons, S. & Pulham, C. R. (2003). *Chem. Commun.* pp. 3004–3005.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
McGregor, P. A., Allan, D. R., Parsons, S. & Pulham, C. R. (2005). *Acta Cryst.* B**61**, 449–454.
Merrill, L. & Bassett, W. A. (1974). *Rev. Sci. Instrum.* **45**, 290.
Moggach, S. A., Allan, D. R., Morrison, C. A., Parsons, S. & Sawyer, L. (2005). *Acta Cryst.* B**61**, 58–68.
Nelmes, R. J., Allan, D. R., McMahon, M. I. & Belmonte, S. A. (1999). *Phys. Rev. Lett.* **83**, 4081–4084.
Oswald, I. D. H., Allan, D. R., Day, G. M., Motherwell, W. D. S. & Parsons, S. (2005*a*). *Acta Cryst.* B**61**. In the press.
Oswald, I. D. H., Allan, D. R., Motherwell, W. D. S. & Parsons, S. (2005*b*). *Acta Cryst.* B**61**, 69–79.
Parsons, S. (2004). *SHADE.* The University of Edinburgh, UK.
Peresypkina, E. V. & Blatov, V. A. (2000*a*). *Acta Cryst.* B**56**, 501–511.
Peresypkina, E. V. & Blatov, V. A. (2000*b*). *Acta Cryst.* B**56**, 1035–1045.
Rute, M. A., Salud, J., Lopez, D. O., Tamarit, J. Li., Negrier, Ph., Barrio, M. & Mondieig, D. (2003). *Chem. Mater.* **15**, 4725–4731.
Sheldrick, G. M. (2001). *SADABS.* University of Göttingen, Germany, and Bruker AXS, Madison, Wisconsin, USA.
Siemens (1995). Area-Detector Integration Software. Siemens Industrial Autom., Madison, Wisconsin, USA.
Spek, A. L. (2004). *PLATON.* Utrecht University, The Netherlands.
Tamarit, J. Ll., Pérez-Jubindo, M. A. & de la Fuente, M. R. (1997). *J. Phys. Condens. Matter*, **9**, 731–737.
Taylor, R. & Macrae, C. F. (2001). *Acta Cryst.* B**57**, 815–827.
Timmermans, J. (1938). *J. Chim. Phys.* **35**, 331.
Watkin, D. J., Pearce, L. & Prout, C. K. (1993). *CAMERON.* Chemical Crystallography Laboratory, University of Oxford, England.