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Pressure-freezing with conformational conversion of 3-aminopropan-1-ol molecules

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3-Aminopropan-1-ol, $NH_2(CH_2)_3OH$, was pressure-frozen and its structure determined at 0.2, 0.9 and 1.31 GPa by single-crystal X-ray diffraction. The freezing pressure of 0.13 GPa at 296 K was measured by ruby fluorescence in the diamond–anvil cell and from compressibility measurement in the piston-and-cylinder reaction press. The molecules assume an extended conformation in the crystalline state, different from the pseudo-ring conformers, with the terminal groups linked by an intramolecular hydrogen bond, present in the gaseous and liquid states. The polar arrangement in the 3-aminopropan-1-ol crystals is explained in terms of the pattern of intermolecular hydrogen bonds.

1. Introduction

Hydrogen bonding is commonly used to engineer crystal structures with required properties. In particular, it can be used for arranging polar molecules into polar crystals, which are required for optical or electronic applications. However, most polar compounds crystallize with the dipoles in an antiparallel orientation. In this study we investigated the intriguing conformational, structural and thermodynamic properties of 3-aminopropan-1-ol (3AP). Because of its characteristic molecular structure comprising a flexible alkane chain with two terminal functional groups, each prone to form hydrogen bonds, the conformation of the 3-aminopropan-1-ol molecule strictly depends on the intra- and intermolecular interactions. In the liquid and gas phases, the 3-aminopropan-1-ol molecules assume pseudo-ring conformations, with the terminal groups linked by an intramolecular hydrogen bond. 3-Aminopropan-1-ol has been extensively studied by microwave spectroscopy and electron diffraction (McMahan *et al.*, 1979; Iijima & Unno, 1998) and by differential scanning calorimetry (DSC), Raman spectroscopy and low-temperature powder X-ray diffraction (Cacela *et al.*, 2003). Its molecular structure has also been predicted by various theoretical methods (Cacela *et al.*, 2000).

Because of its short alkane chain and terminal amino and hydroxyl groups, 3-aminopropan-1-ol is a model example of an amino-alcohol. In the series of $NH_2(CH_2)_nNH_2$ and $OH(CH_2)_nOH$ compounds with increasing tether length, the melting points increase with systematically higher values for even n and lower values for n odd, and with the lowest melting points for the propane ($n = 3$) derivatives (Thalladi *et al.*, 2000; Boese *et al.*, 1999). In these studies the melting points were correlated to the molecular packing and interactions in the crystalline state. It was also shown that the crystal symmetry depends on the n parity: for n even $NH_2(CH_2)_nNH_2$ crystallizes in space group *Pbca* and for n odd in space group *Cmc*2_1, with the exception for $n = 2$ as all polymorphs of 1,2-

diaminoethane crystallize in space group $P2_1/c$ (Budzianowski *et al.*, 2006). Diols OH(CH$_2$)$_n$OH exist in space group $P2_1/n$ for *n* even (except $P2_12_12_1$ for *n* = 2 and $P2_1/c$ for *n* = 10) and in space group $P2_12_12_1$ for *n* odd (except $P2_1/c$ for *n* = 3). It can be noted that the empirical rule that the centrosymmetric crystals have higher density than the non-centrosymmetric crystals is fulfilled for the *n*-diamines and *n*-diols, which is related to the molecular structure in this series of compounds.

In the diamines there is an excess of H-atom donors for hydrogen bonds over the H-atom acceptor sites (four *versus* two), whereas the reverse ratio occurs in diols. In amino-alcohols this ratio is balanced (three H-atom donors and three H-atom acceptor sites). The NH$_2$ and OH groups can form homonuclear O—H$\cdots$O and N—H$\cdots$N, and heteronuclear N—H$\cdots$O and O—H$\cdots$N intra- and also intermolecular hydrogen bonds. The influence of the varied OH and NH$_2$ groups on molecular symmetry is still being investigated in NH$_2$(CH$_2$)$_n$OH and mixtures of diamines with diols (Budzianowski *et al.*, 2006). A characteristic feature of the NH$_2$(CH$_2$)$_3$OH molecule, compared with the diamines and diols, is the contribution of the different terminal groups to the molecule's polarity. The association of the polar molecules can lead to strongly polar structures.

The conformation of the 3AP molecule can be described by a sequence of four torsion angles, H—O—C—C, O—C—C—C, C—C—C—N and C—C—N—L (L represents the lone electron pair of N), or the equivalent conformation descriptors (lower-case symbols g^+ for *gauche*$^+$, g^- for *gauche*$^-$ and *t* for *trans* for H—O—C—C and C—C—N—L; and the analogous

capital-letter symbols G^+, G^- and T for torsion angles O—C—C—C and C—C—C—N). It was shown by FT-IR spectroscopy and DFT (density functional theory) *ab initio* calculations (Przesławska *et al.*, 1999) that in the gaseous phase 3AP exists as a mixture of conformers. In the lowest energy conformers a six-membered pseudo-ring is closed by an intramolecular O—H$\cdots$N hydrogen bond (Iijima & Unno, 1998). This molecular form is described as the $g^-G^+G^-g^+$ conformer. In pure liquid, where intermolecular hydrogen bonds are also formed, the role of the intramolecular hydrogen bond diminishes and acyclic 3AP conformers are more likely. The Raman and IR spectra of liquid 3-aminopropan-1-ol resemble the spectra calculated [by HF (Hartree–Fock) and MP2 (Møller–Plesset perturbation theory second order) methods] for the $g^-G^-G^+g^+$ conformer with a weak intramolecular N—H$\cdots$O bond (Cacela *et al.*, 2000).

At low temperature, Cacela *et al.* (2003) observed and tentatively characterized, by powder X-ray diffraction, two polymorphs of 3AP and its amorphous state. At varied temperature, a sequence of diffraction patterns first shows the amorphous state at 153 K, then the metastable form II at 208 K, and finally phase I at 243 K. The formation of the metastable crystal II always anticipated the formation of stable polymorph I, testifying to a monotropic relation between 3-aminopropan-1-ol polymorphs, meaning that over the entire temperature range below the melting point polymorph I is more stable than II.

This study was undertaken to determine the molecular structure of 3AP in the crystalline phase. We were primarily interested in the intermolecular and intramolecular interactions, the type of hydrogen bonds formed, the molecular conformation and the supramolecular structure of this compound, both at low temperature and high pressure. To our knowledge, the crystal structure of 3AP has not been determined; only the unit-cell dimensions of the stable low-temperature polymorph measured by powder X-ray diffraction have been reported. Hence, we commenced our structural investigations at high pressure, to establish if new polymorphs can be obtained in this way.

2. Experimental

At ambient conditions, 3-aminopropan-1-ol is a highly hygroscopic liquid, freezing at 283–285 K. We pressure-froze the liquid in a modified Merrill & Bassett (1974 diamond–anvil cell (DAC). The gasket was made of 0.3 mm steel foil and the initial diameter of the spark-eroded hole was 0.5 mm. The pressure was calibrated with a BETSA PRL spectrometer by the ruby-fluorescence method with a precision of 0.05 GPa (Piermarini *et al.*, 1975). The pressure in the DAC chamber with 3-aminopropan-1-ol was gradually increased until the sample froze in the polycrystalline form. Then the DAC was heated until all the crystallites but one melted, after which the temperature was slowly lowered and this single crystal grew to entirely fill the pressure chamber at room temperature (Fig. 1).

A single crystal of 3AP was centred on a Kuma KM4 CCD diffractometer by the gasket-shadow method (Budzianowski
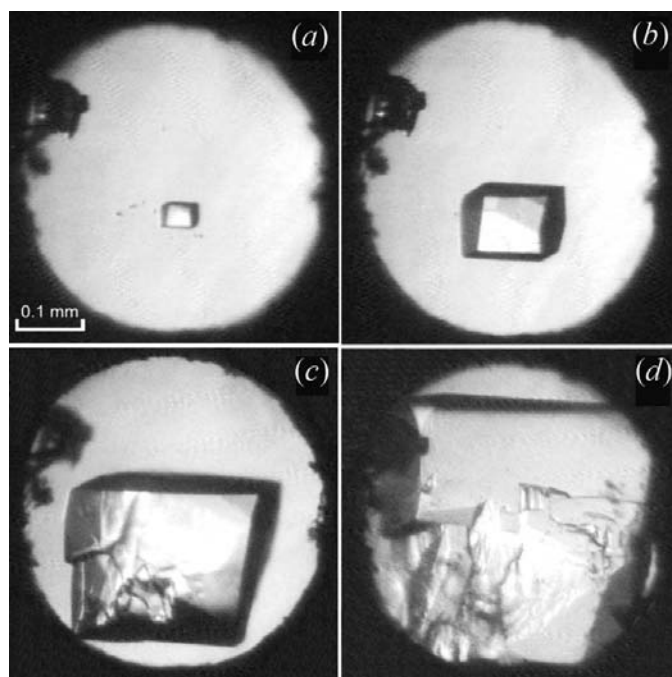

Figure 1
Stages of the 3AP single-crystal isochoric growth in the DAC chamber: (*a*) one 3AP seed at 367 K; (*b*, *c*) the crystal size gradually increasing with lowering temperature; (*d*) the crystal nearly filling the whole chamber volume at 320 K and 0.25 GPa. The ruby chip for pressure calibration is at the upper-left edge of the chamber.

Table 1
Selected experimental and crystal data for the high-pressure structure of 3-aminopropan-1-ol at 0.20, 0.90 and 1.31 GPa.

Pressure	0.20 GPa (1)	0.90 Gpa (2)	1.31 GPa (3)
Crystal data			
Chemical formula	C_3H_9NO	C_3H_9NO	C_3H_9NO
M_r	75.11	75.11	75.11
Cell setting, space group	Monoclinic, Cc	Monoclinic, Cc	Monoclinic, Cc
Temperature (K)	296	296	296
a, b, c (Å)	5.932 (4), 8.259 (5), 8.598 (5)	5.853 (5), 8.123 (10), 8.428 (3)	5.829 (2), 8.052 (5), 8.343 (3)
β (°)	93.64 (5)	91.99 (5)	91.67 (3)
V (Å^3)	420.4 (4)	400.4 (6)	391.4 (3)
Z	4	4	4
D_x (Mg m^{-3})	1.187	1.246	1.275
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.09	0.09	0.09
Crystal form, colour	Disc, colourless	Disc, colourless	Disc, colourless
Crystal size (mm)	$0.49 \times 0.42 \times 0.24$	$0.43 \times 0.40 \times 0.24$	$0.42 \times 0.39 \times 0.23$
Data collection			
Diffractometer	Kuma KM4 CCD	Kuma KM4 CCD	Kuma KM4 CCD
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Analytical	Analytical	Analytical
T_{min}	0.67	0.43	0.67
T_{max}	0.97	0.86	0.96
No. of measured, independent and observed reflections	940, 271, 254	1199, 334, 284	814, 240, 219
Criterion for observed reflections	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$
R_{int}	0.039	0.066	0.035
θ_{max} (°)	27.7	25.0	28.7
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.110, 1.13	0.044, 0.122, 1.09	0.029, 0.091, 1.23
No. of reflections	271	334	240
No. of parameters	52	58	58
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2 (F_o^2) + (0.0739P)^2 + 0.1334P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2 (F_o^2) + (0.0868P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2 (F_o^2) + (0.0671P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	< 0.0001	0.429	0.196
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.09, −0.08	0.08, −0.09	0.08, −0.09

Computer programs: *CrysAlis* (Oxford Diffraction, 2003), *SHELXS*97 and *SHELXL*97 (Sheldrick, 2008), *X-SEED* (Barbour, 2001).

& Katrusiak, 2004). The Mo $K\alpha$ radiation from the sealed X-ray tube was graphite monochromated. The X-ray reflection intensities were collected in the ω-scan mode (Budzianowski & Katrusiak, 2004). The *CrysAlis* programs (Oxford Diffraction, 2003) were used for data collection, unit-cell refinement and initial data reduction. The data were corrected for the DAC absorption, gasket shadowing and absorption of the sample itself (Katrusiak, 2003, 2004). The structure was solved by direct methods using the program *SHELXS97* and refined using *SHELXL97* (Sheldrick, 2008). The molecular graphics were computed by *X-SEED* (Barbour, 2001). The C, O and N atoms were refined with anisotropic displacement parameters. The amine and hydroxyl H atoms were located from Fourier maps and refined with isotropic U factors, whereas the methylene H atoms were calculated from molecular geometry [C—H = 0.97 Å and U_{iso}(H) = $1.2U_{eq}$(C)]. In the subsequent experiments, pressure in the DAC was increased to 0.90 and 1.31 GPa, and single crystals were again obtained by isochoric crystallization. The structure at 0.2 GPa was applied as the

starting model for refining the structures at higher pressures. The measurements at 0.2 and 1.13 GPa were performed in a DAC with the diamond–anvil cells supported by steel backing plates with conical windows (Katrusiak, 2008), and the measurement at 0.9 GPa in a DAC with a backing plate of beryllium.

The crystal structure of 3AP is pseudo-symmetric, and it approximates the space group $C2/c$ with the exception of the atomic types and H-atom sites of the NH$_2$ and OH groups. The higher symmetry of $C2/c$ would require that the molecules be located on a twofold axis parallel to [y], and consequently, that the NH$_2$ and OH groups be 50:50 disordered. On the other hand, the reversal of the NH$_2$ and OH groups leads to the same structure with the reversed polar axis, and can be distinguished by the anomalous dispersion. After assigning the N and O atoms, the H atoms appeared in the difference Fourier maps consistent with this assignment, and the displacement parameters of N and O refined to similar amplitudes. Also, better reliability factors were obtained for the structure

Table 2
Molecular dimensions (Å, °) of 3-aminopropan-1-ol at varied pressure (GPa) in the crystalline state (this work) and in vapour (Iijima & Unno, 1998).

	0.2 GPa	0.9 GPa	1.31 GPa	Vapour
C—C	1.512 (12)	1.535 (15)	1.524 (15)	1.537 (2)
C—O	1.428 (8)	1.429 (10)	1.492 (11)	1.425 (3)
C—N	1.473 (7)	1.490 (13)	1.430 (14)	1.469 (3)
C—C—C	112.5 (3)	110.6 (4)	111.2 (4)	113.2 (3)
C—C—O	113.0 (4)	111.3 (6)	107.4 (4)	111.9 (4)
C—C—N	110.6 (4)	109.4 (8)	114.1 (9)	112.0 (4)
C—C—C—N	178.8 (4)	177.7 (4)	178.3 (4)	−57.0 (2)
C—C—C—O	177.3 (6)	178.8 (4)	177.5 (4)	72.1 (8)

Figure 4
The pressure dependence of molecular volume (V_m) of 3AP measured in the piston-and-cylinder device (blue points and lines) and in the crystalline state by X-ray diffraction in the Merrill–Bassett DAC (red triangles), at 243 K (red square). The freezing pressure of 0.13 GPa has been estimated from the V_m compression.
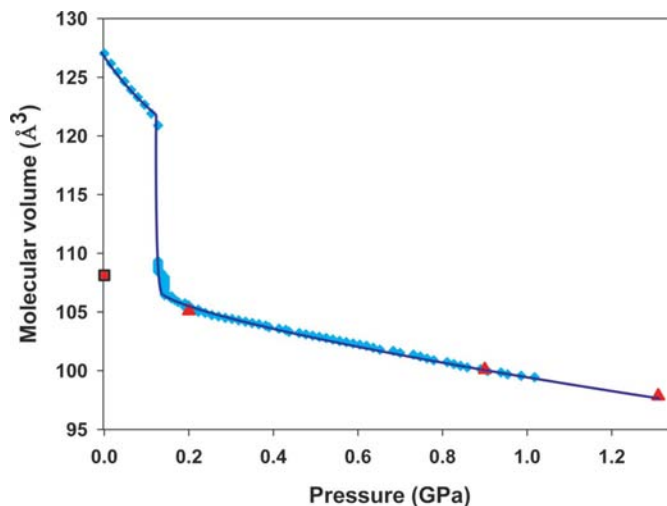
refined with the NH₂ and OH groups ordered than for the disordered model. For example, the refinement of the disordered structure in space group $C2/c$ at 1.31 GPa gave $R1 = 0.044$ (cf. Table 1). It was additionally noted for the intermolecular hydrogen bonds that all Donohue angles deviate to a greater extent from the ideal tetrahedral values of 109° for the acceptor groups, and to a lesser extent for the donor groups, which is consistent with the knowledge on hydrogen bonds. The accuracy of the high-pressure experiment could, to some extent, be obscured by high background from the DAC, but otherwise there is a series of facts (location of H atoms, displacement amplitudes, R factors, Donohue angles) confirming the polar space group Cc for the 3AP crystal.
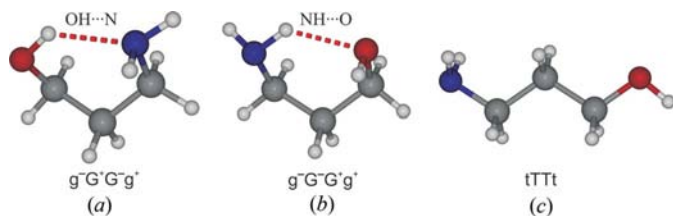
Figure 2
Structural diagrams showing the different conformations of the molecule identified in the (*a*) gas and (*b*) liquid phases, and (*c*) the crystal at high pressure.
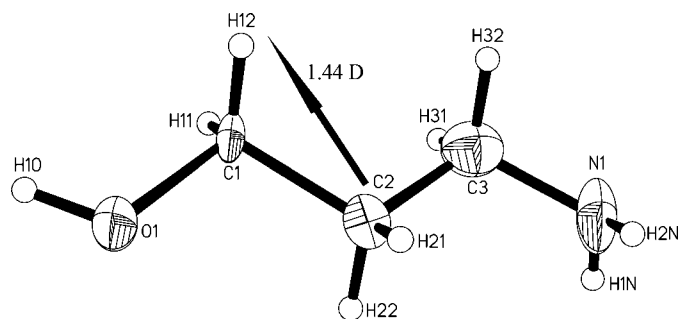
Figure 3
The molecule of 3-aminopropan-1-ol as determined in the crystal structure at 1.3 GPa. The displacement ellipsoids have been drawn at the 50% probability level. The arrow indicates the direction of the calculated dipole moment of the molecule, and its magnitude has been given as 1.44 debye = 4.804 × 10⁻³⁰ Cm (1 debye = 3.336 × 10⁻³⁰ Cm).

The compressibilities of liquid and solid 3AP were measured in a piston-and-cylinder apparatus, similar to that described by Baranowski & Moroz (1982), at 296 K. The freezing pressure of 0.13 GPa at 296 K was determined from the anomaly in this molecular-volume measurement. The calculations of the molecular dipole moment were performed with the program *GAUSSIAN03* (Frisch *et al.*, 2003) at the B3lyp/6–311++G(d, p) level of theory.

3. Discussion

3.1. Crystal symmetry

Both low-temperature polymorphs observed by X-ray powder diffraction belong to the monoclinic system (Cacela *et al.*, 2003). Cacela *et al.* established that the unit cell of polymorph I is *C*-centred, its volume is 432.52 Å³ at 243 K and it contains four molecules. The unit-cell parameters of polymorph I, determined by Cacela *et al.* (2003), $a = 5.945$ (2), $b = 8.403$ (3), $c = 8.678$ (3) Å and $\beta = 93.85$ (3)°, are similar and systematically slightly larger than the corresponding values measured for 3AP at 0.2 GPa (see Table 1[1]). Thus, based on the unit-cell dimensions, we conclude that isobaric freezing at 243 K and isochoric freezing at 0.2 GPa lead to the same phase I of 3AP.

3.2. Molecular conformation

The conformation of the 3-aminopropan-1-ol molecule (see Fig. 2) can change due to torsions around the O1—C1, C1—C2, C2—C3 and C3—N1 single bonds. The corresponding dihedral angles are expected to be close to either 60°, −60° or 180°. The calculations aimed at energy minimization for the

isolated molecule revealed the conformers with intramolecular hydrogen bonds (Cacela *et al.*, 2000). In the gas phase and for the matrix-isolated compound the most stable conformer is $g^-G^+G^-g^+$, whereas in liquid the most populated conformer is $g^-G^-G^+g^+$. In the crystal structure, determined in this study, the molecule of 3-aminopropan-1-ol assumes an 'open' form of conformer *tTTt* (Fig. 3), labelled number 10 in the sequence arranged according to increasing energy (Przesławska *et al.*, 1999).

The values of torsion angles in the N1—C3—C2—C1—O1 chain (Table 2) deviate up to a mere 2.5° from the 180° angle, associated with the idealized planar conformation. Thus, the backbone of the molecule is nearly flat, and deviations of the C, N and O atoms from the plane fitted to all non-H atoms do not exceed 0.021 (2) Å in any of the high-pressure structures. The geometrical parameters of the molecule are presented in Table 2. The conformation of the amine group (*i.e.* the location of the H atoms) is consistent with that observed in the 1,2-diaminoethane polymorphs (Budzianowski *et al.*, 2006).

Isothermal freezing of 3AP at 0.13 GPa is accompanied by a considerable transition volume jump of −12% (Fig. 4). Such a significant volume change was not observed in our previous experiments. This volume change may be connected, to some extent at least, with the conformational transformations of molecules. It was shown by Cacela *et al.* (2000) that the pseudo-cyclic conformation prevails in the liquid state, and the molecule in this conformation encloses a volume inside the pseudo-ring which is eliminated in the extended conformation.

3.3. Hydrogen bonds and intermolecular interactions

The enclosure of an intramolecular hydrogen bond stabilizing the six-membered pseudo-cyclic conformer requires that all torsion angles be close to *gauche*. The formation of the pseudo-ring may, in principle, involve one of three hydrogen-bonding sites associated with the hydroxyl and one of three sites of the amine group. There is one possible configuration
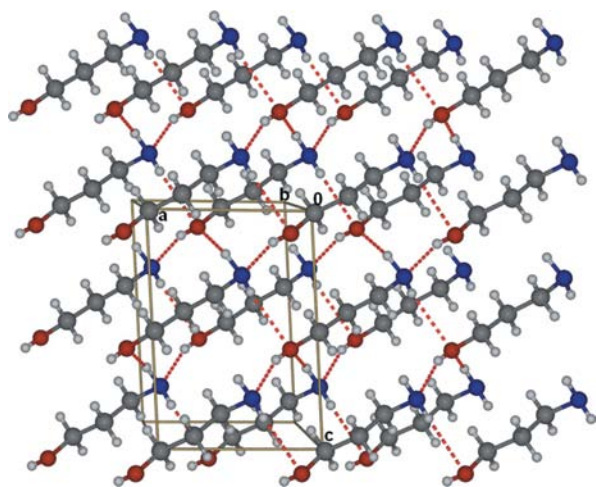
Table 3
Dimensions of intermolecular hydrogen bonds (Å, °) in the crystal of #AP at varied pressure.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D-H\cdots A$	$D\cdots A$
Pressure 0.2 GPa				
O1—H1···N1[i]	0.820	2.018	162.16	2.811 (5)
N1—H1···O1[ii]	1.03 (8)	2.33 (6)	146 (8)	3.239 (7)
N1—H2···O1[iii]	0.86 (7)	2.54 (9)	139 (10)	3.239 (6)
Pressure 0.9 GPa				
O1—H1···N1[i]	1.00 (5)	1.81 (6)	162 (6)	2.778 (5)
N1—H1···O1[ii]	0.85 (5)	2.33 (6)	168 (6)	3.168 (6)
N1—H2···O1[iii]	0.80 (6)	2.46 (5)	144 (6)	3.141 (5)
Pressure 1.31 GPa				
O1—H1···N1[i]	0.97 (7)	1.82 (8)	167 (11)	2.763 (5)
N1—H1···O1[ii]	0.90 (5)	2.26 (6)	165 (6)	3.134 (5)
N1—H2···O1[iii]	0.78 (6)	2.47 (5)	140 (5)	3.104 (4)

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

allowing the formation of an intramolecular O—H···N bond, and four such configurations if an N—H···O bond were to be formed. In the gaseous phase the first and second lowest energy forms correspond to the conformers with an intramolecular O—H···N hydrogen bond (Cacela *et al.*, 2000). In the pure liquid the third most stable form with an intramolecular N—H···O bond ($g^-G^-G^+g^+$) was identified. The strength of the groups varies with the charges induced in the H-atom donor and H-atom acceptor atoms. These charges, in turn, are stabilized according to the electronegativity of the atoms concerned. This is consistent with the O—H···N bond being stronger than the N—H···O (McMahan *et al.*, 1979). The conformation assumed by 3AP molecules in the crystalline state is optimum for the formation of intermolecular hydrogen bonds.

The closest intermolecular contacts in the 3AP crystal involve all the H-atom donor and H-atom acceptor sites of the OH and NH$_2$ groups (Table 3, Fig. 5). Except for H1 at

Figure 5
Autostereographic projection (Katrusiak, 2001) of the 3AP crystal structure viewed down *b*. The hydrogen bonds are indicated by dashed lines.
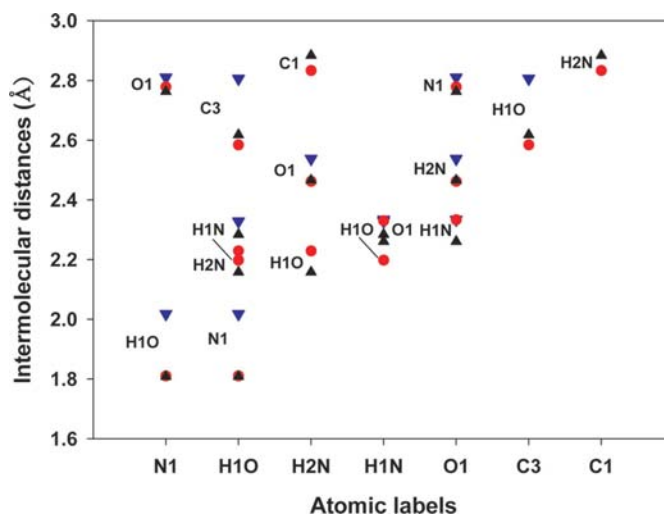

Figure 6
The closest intermolecular distances in the crystal of 3AP at high pressure (blue triangles down for 0.2 GPa, red circles for 0.9 GPa and black triangles up for 1.31 GPa). Only the distances shorter than the sums of the van der Waals radii (Bondi, 1964) of corresponding atoms have been presented (hydrogen–hydrogen contacts have been excluded).

0.2 GPa, all amino and hydroxyl H atoms were located from the difference Fourier maps and refined; H1 at 0.2 GPa was calculated from molecular geometry at the fixed O—H distance of 0.82 Å.

The next shortest are the distances between the C atoms adjacent to the OH and NH_2 groups and the acidic protons of the neighbouring molecules, as illustrated in the plot of shortest intermolecular distances in Fig. 6, by the colour scale related to the van der Waals radii of interacting atoms on the Hirshfeld surface in Fig. 7 (McKinnon *et al.*, 2007).

It is apparent that a supramolecular structure is formed in the 3AP crystals due to OH···N and NH···O bonds, while the central part of the alkane moiety does not form short contacts. The existence of weak interactions beyond van der Waals radii was recently shown for 1,1-dichloroethane (Bujak *et al.*, 2008) and postulated for molecular crystals (Dance, 2002).

The map of intermolecular contacts on the Hirshfeld surface in Fig. 8 shows that, according to increasing pressure, only the ends of the molecular chain are influenced significantly.

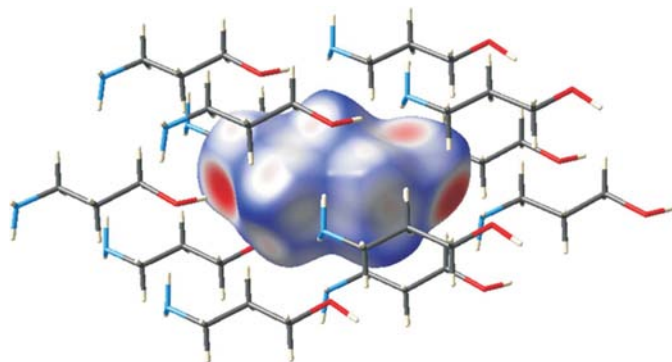Molecules of 3AP, each hydrogen bonded to six neighbours, form a three-dimensional network. In the solid state, the chains of 3-aminopropan-1-ol molecules are connected by O—H···N bonds. All the chains are parallel (Fig. 9). The weak N—H···O hydrogen bonds linking collateral chains (Fig. 3) are essential for the parallel orientation of the chains in the crystal.

3.4. Polar arrangement of molecules

The systematic dependence of crystal symmetry on the tether-chain length in normal diols and diamines testifies that the orientation of H-atom donors and H-atom acceptors is essential for the molecular arrangement. In the 3AP structure the molecules are OH···N-bonded into chains, and the chains are arranged parallel along [201] owing to the specific orientation of the H-atom donor and H-atom acceptor sites of two symmetry-independent hydrogen bonds. The two symmetry-independent NH···O bonds are directed in this way, that only parallel orientations of the OH···N-bonded chains are favoured. The network of NH···O bonds extends in two dimensions, approximately perpendicular to the OH···N-bonded chains and therefore the molecules are aligned parallel in the crystal.

The molecular arrangement is also favourable for the electrostatic interactions in the 3AP structure. The dipole moment of the 3AP molecule is inclined by *circa* 60° to the intramolecular N···O direction (Fig. 3). The dipole-moment component perpendicular to the N···O line in the molecule along crystal axis [y], $\mu_{[y]}$, is approximately twice as long as the $\mu_{[201]}$ component nearly parallel to the intramolecular O···N line lying along crystal direction [201]. The $\mu_{[y]}$ component is almost 1.7 times larger than $\mu_{[201]}$, and the molecules are arranged in the crystal lattice in such a way that the larger $\mu_{[y]}$ components of the dipole moments compensate ($\mu_{[y]}$ is perpendicular to the glide planes *c* and *n*), whereas the smaller $\mu_{[201]}$ components are all parallel, due to the stabilizing effect of the NH···O bonds, as explained above.

Figure 7
Hirshfeld surface for the 3AP molecule in the centre of its coordination sphere, shown in the wireframe style, in the crystal structure at 1.3 GPa. The colour scale on the surface (McKinnon *et al.*, 2007) represents distances from the surface elements to the closest atoms normalized to the sum of their van der Waals radii (red colour corresponds to the shortest contacts, blue to the longest). The Hirshfeld surface was plotted with the program *CrystalExplorer* (Wolff *et al.*, 2007).
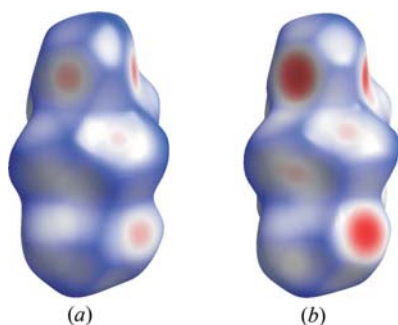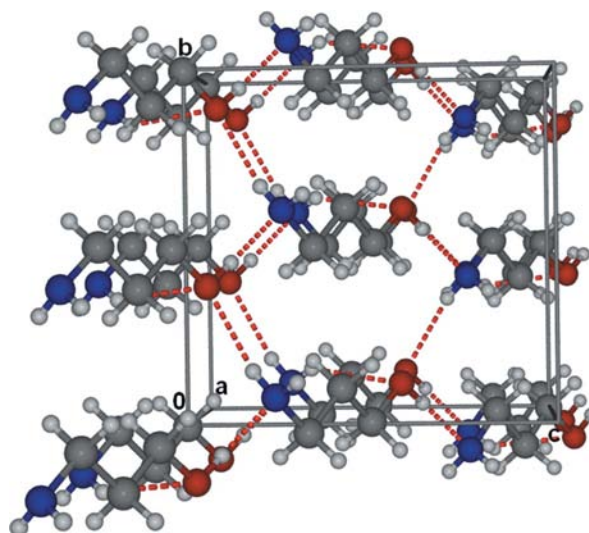

Figure 8
Normalized intermolecular contacts (McKinnon *et al.*, 2007) mapped on the Hirshfeld surfaces of the 3AP molecule compared for the crystal structures at (*a*) 0.2 GPa and (*b*) 1.3 GPa.

Figure 9
The molecular arrangement of 3-aminopropan-1-ol viewed down [*x*].

4. Conclusions

Molecules of 3-aminopropan-1-ol transform their conformation between solid, gas and liquid phases. The conformers are stabilized by the hydrogen bonds specific for different conformations of the molecule. In the pseudo-ring conformation the hydrogen bonds have to compete with the strains imposed by the molecular geometry and sterical hindrances, preventing all the H-atom donors and H-atom acceptors from forming hydrogen bonds. Although energetically unfavourable for the isolated molecule, the extended conformation is preferred in the condensed 3AP, because it allows all H-atom donors and acceptors to be involved in intermolecular hydrogen bonding and eliminates the void enclosed inside the pseudo-ring. The location of the amine and hydroxyl groups is essential for the polar arrangement of the molecules in the crystal.

References

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