CrystEngComm

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

ARTICLE TYPE www.rsc.org/xxxxxx | XXXXXXXX

Low-Temperature and High-Pressure Polymorphs of Isopropyl Alcohol

Joe Ridout[a] and Michael R. Probert*[b]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b00000000x

Single-crystal X-ray diffraction has been used to elucidate the structure of two polymorphs of isopropyl alcohol, one grown through *in-situ* cryo-crystallisation, the other through high-pressure crystallisation. The packing in both structures is dominated by O-H···O hydrogen bonds, with the high-pressure polymorph being significantly more dense than the low-temperature structure.

Introduction

Isopropyl alcohol is a very important laboratory chemical, employed as a low-boiling polar protic solvent. Despite the ubiquitous use of isopropyl alcohol in chemistry laboratories worldwide, no crystallographic structure has been hitherto reported. There are two principle techniques for crystallising a liquid, namely cryo-crystallisation at ambient-pressure, and high-pressure crystallisation at ambient-temperature.[1]

It is well known that high-pressure crystallisation of liquids sometimes generates different polymorphs to those seen through cryo-crystallisation. Examples include water ice,[2] benzene,[3] phenol,[4] acetone,[5] 1,2-dichloroethane,[6] monofluorotoluene,[7] 4-fluorophenol,[8] chlorotrimethylsilane[9] and 1-bromo-2,4,6-trifluorobenzene.[10] This is interesting as it provides an alternative way to study intermolecular interactions in simple systems. Furthermore, kinetic variations in either freezing technique, such as the rate of cooling or compression may further increase the diversity of polymorphs obtained.[11,12]

Crystal structures of such simple solvents are useful for several reasons. Firstly, the simplicity of typical solvent molecules allows one to isolate and understand the effect of a particular intermolecular interaction on the packing of molecules.[13] Secondly, low melting-point liquids such as isopropyl alcohol represent an interesting method through which one can study the different effects of temperature and pressure. This is because the two crystallisation conditions (cryo-crystallisation and high-pressure crystallisation) are thermodynamically distinct, with large deviations of pressure or temperature from ambient conditions needed to freeze the solvent molecules. Thirdly, free energy calculations utilizing a solvent crystal structure may be used to computationally predict the formation of solvates of a particular molecule.[14,15]

Herein, we report and discuss the low-temperature and high-pressure polymorphs of isopropyl alcohol.

Experimental Section

The low-temperature crystal form was obtained by filling a Lindemann capillary with pure isopropyl alcohol and sealing the tube. This was attached it to a modified mount[16] fitted to the omega circle of a Bruker AXS 6K X-ray diffractometer. The sample was then cooled at 360 Kh^{-1} to 120 K, left at this temperature for 10 minutes, and then warmed at 360 Kh^{-1} to 180 K to induce crystallisation. A single crystal of suitable quality was then isolated through rapid temperature cycling between 183 and 185 K at 360 Kh^{-1}. This temperature cycling about the melting point (184 K) resulted in the growth of larger crystals whilst melting the smaller crystals.

The high-pressure polymorph was grown in a diamond anvil cell, with a 0.8 mm culet, using a stainless steel gasket. A sample chamber of diameter 0.3 mm was drilled through the gasket. Pure isopropyl alcohol and a ruby chip were then added to the chamber. Compression alone was not sufficient to induce crystallisation, therefore a modified strategy was employed.

The diamond anvil cell containing the sample at ambient pressure was immersed in liquid nitrogen for approximately five minutes to induce crystallisation, forming a powder. The cell was then removed from the liquid nitrogen, and before the crystalline sample could melt, an over-pressure was applied. The sample was then allowed to slowly warm to room-temperature over approximately 20 minutes. Pressure-cycling around the melting point isolated a suitable single crystal grown from the powder seeds. The cell was then left for approximately 24 hours for the pressure to equilibrate and then the pressure was measured using the Ruby R_1 fluorescence method.[17] The pressure was measured at 11.2 (2) Kbar.

Very low melting point compounds can often provide challenges during crystallisation. We find that this is more commonly observed for the cryogenic conditions due to the delay between and observation and temperature manipulation. In our experience, however, if a compound can be induced to form a microcrystalline powder phase, it is almost always possible to isolate a suitable single crystal, given enough time and patience. One particularly fruitful method for the most challenging systems is to warm the microcrystalline sample to one or two Kelvin below the melting point and apply a zone melting technique, either as described by Boese and Nussbaumer using an OHCD laser[18] or by touching the bottom end of the capillary to melt all but a thin layer of crystals at

the top of capillary and leaving the system for a couple of hours for crystals to grow down the capillary. If crystal growth is too rapid, and an excess of small crystals is formed then the process should be repeated at a slightly higher temperature.

High-pressure data were collected using XIPHOS II,[19] a diffractometer that has been custom-built for the collection of high-pressure X-ray diffraction images. This diffractometer forms part of the XIPHOS diffraction facility[20] currently based at Newcastle University. XIPHOS II uses an Incoatec Ag IμS system[21] for generating X-rays. The shorter wavelength radiation produced by Ag is advantageous for high-pressure diffraction experiments for two principle reasons. Firstly, it reduces the absorption of the X-radiation by the diamond anvils. Secondly, it allows for more data to be collected within the restricted geometrical constraints of the body of the cell.

ECLIPSE[22] was used to produce files masking areas of the high-pressure diffraction pattern occluded by the body of the diamond anvil cell. SAINT[23] and SADABS[24] were used (as part of the APEX2 software suite[25]) for the integration and scaling of data respectively. The SHELX software suite of programs[26] was used for solution and least squares refinement of the data, within the Olex2 GUI.[27]

Results and Discussion

The low-temperature polymorph was found to crystallise in space group $P2_1/c$, Z'=3, with 1-dimensional helical chains of O-H···O hydrogen bonds along the *a* axis. It is well known that monoalcohols have a tendency to crystallise with a Z' value greater than 1,[28] with Z'=3 being especially common as it allows for the formation of a hydrogen-bonded helix without the side chains having to match in a symmetric fashion. The helical hydrogen-bonding motif in the low-temperature structure of isopropyl alcohol is shown in figure 1, and the full crystal structure is shown in figure 2.

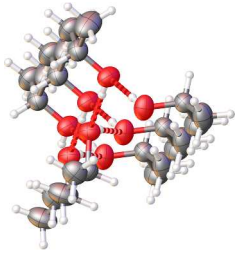

Fig. 1. One-dimensional helical chain of hydrogen-bonding in the low-temperature polymorph of isopropyl alcohol.

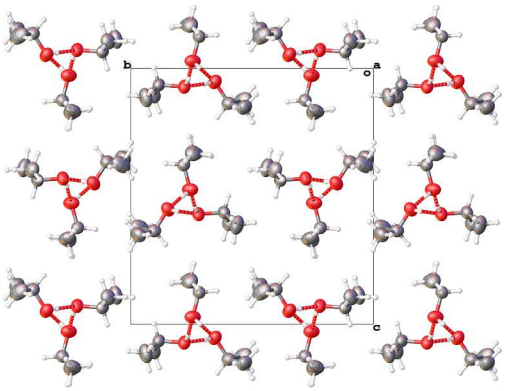

Fig. 2. Crystal structure of the low-temperature polymorph of isopropyl alcohol crystal structure, showing 1-dimensional helical chains down the *a* axis.

The high-pressure polymorph was also found to crystallise in a high Z' structure, this time with Z'=4, in space group $P2_1/c$. We see a very different arrangement of hydrogen bonds in this structure, with isolated 8-membered rings formed. Secondary alcohols are known to form rings and chains with approximately equal propensity,[29] and it is satisfying to see that isopropyl alcohol will adopt either motif depending on the crystallisation conditions.

The eight-membered ring seen in the high-pressure polymorph is shown in figure 3.

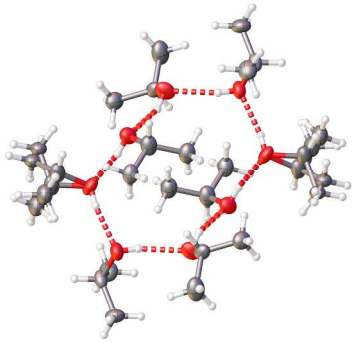

Fig. 3. Hydrogen-bonded ring in the high-pressure polymorph.

One of the four independent molecules in the high-pressure structure is disordered, with the side chain having two possible orientations, with refined occupancies of ≈ 0.5 in both positions.

The full crystal structure of the high-pressure polymorph is shown in figure 4.

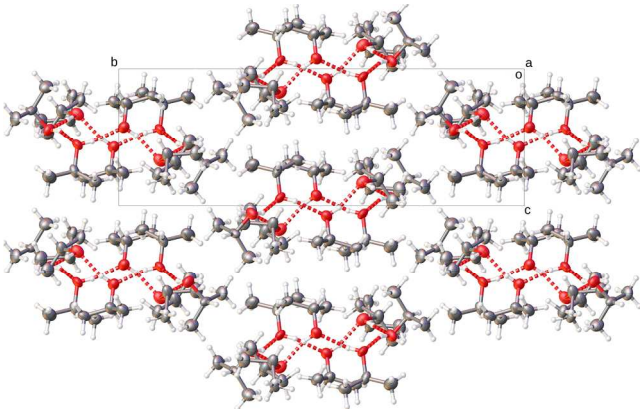

Fig. 4. Crystal structure of the high-pressure polymorph of isopropyl alcohol, viewed down the *a* axis.

One can see that the eight membered rings in the high-pressure polymorph are closely-packed, but with no strong intermolecular interactions between each ring.

Comparison of the structures of isopropyl alcohol to the simplest alcohols, methanol and ethanol, is interesting. In methanol, the high-pressure structure has more strained hydrogen-bonding interactions than the low-temperature structure. These strained interactions are tolerated in order to achieve a greater packing efficiency.[30] However, in ethanol, the high-pressure structure has more linear hydrogen bonding interactions than the low-temperature structure.[31] (It should, however, be noted that the high-pressure form has highly distorted C-O and C-C bond lengths in order to achieve both a high-packing efficiency and a linear hydrogen-bonding network.[31])

The C-C and C-O bond lengths in the two polymorphs of isopropyl alcohol do not differ significantly. The length and directionality of hydrogen-bonds and densities of both polymorphs of isopropyl alcohol are listed below in table 1.

Table 1 Table showing hydrogen bond lengths and angles and densities of the two polymorphs of isopropyl alcohol.

Polymorph	O···O Distance / Å	C-H···O Angle / °	Density / **gcm^{-3}**
Low-Temperature	2.7190 (12)	174.143 (3)	**0.958**
	2.7222 (12)	172.498 (8)	
	2.7289 (14)	172.561 (2)	
High-Pressure	2.681 (8)	165.8 (4)	**1.131**
	2.709 (7)	154.1 (6)	
	2.711 (7)	166.4 (5)	
	2.733 (7)	156.4 (4)	

It is apparent that the hydrogen bonds in the two structures of isopropyl alcohol are of similar lengths. However, as observed in methanol, the high-pressure bond angles are rather strained and diverge significantly from linearity, with the low-temperature structure having fairly linear hydrogen bonds. The density of the high-pressure phase was found to be approximately 18% higher than that of the low-temperature phase.

Conclusions

Two polymorphs of isopropyl alcohol have been isolated and characterised, one through cryo-crystallisation, the other through a modified high-pressure crystallisation protocol. The two polymorphs have very different packing motifs and densities. The high-pressure polymorph is much denser, with the molecules forming hydrogen bonded rings. In the low-temperature polymorph there are 1-dimensional helical chains of molecules linked by hydrogen bonds.

Acknowledgements

The authors would like to thank Dr. L. S. Price and Dr. E. Pohl for helpful discussions, Prof. A. Beeby for use of a fluorescence spectrometer and to Bruker UK Ltd. and EPRSC for financial support.

Notes and references

[a] *Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, United Kingdom. E-mail: joe.ridout@durham.ac.uk*
[b] *School of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, United Kingdom. E-mail: michael.probert@newcastle.ac.uk*

† Electronic Supplementary Information (ESI) available: CIFs Crystallographic Data See DOI: 10.1039/b000000x/

‡ Summary of Crystallographic Data:
Low-Temperature Polymorph: Chemical formula = C_3H_8O, Formula weight = 60.09, Temperature = 180 (2) K, Pressure = 0.001 Kbar, monoclinic, space group = $P2_1/c$, a = 6.542 (3) Å, b = 13.415 (14) Å, c = 14.469 (11) Å, β = 99.79 (2) °, V = 1251.3 (17) Å^3, Z = 12, Fcalc = 0.958, μ = 0.069 mm^{-1}, unique reflections = 1487, observed reflections = 1369, completeness = 92.1 %, θ_{max} = 21.770, R1 = [I > 2σ] 0.0468, *w*R2 = [all] 0.1231, goodness-of-fit = 1.002.
High-Pressure Polymorph: Chemical formula = C_3H_8O, Formula weight = 60.09, Temperature = 292 K, Pressure = 11.2 (2) Kbar, monoclinic, space group = $P2_1/c$, a = 8.7267 (18) Å, b = 21.838 (6) Å, c = 8.408 (3) Å, β = 118.243 (8) °, V = 1441.6 (7) Å^3, Z = 16, Fcalc = 1.141, μ = 0.052 mm^{-1}, unique reflections = 1234, observed reflections = 743, completeness = 60.2 %, θ_{max} = 15.340, R1 [I > 2σ] = 0.0585, *w*R2 [all] = 0.1429, goodness-of-fit = 1.109.

1. E. V. Boldyreva, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 218-231.
2. V. Petrenko and R. Whitworth. *Physics of Ice*, Oxford University Press: Oxford, U.K., 1999.
3. R. J. Fourme, D. Andre and M. Renaud, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1971, **27**, 1275-1276.
4. D. R. Allan, S. J. Clark, A. Dawson, P. A. McGregor and S. Parsons, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, **58**, 1018-1024.
5. D. R. Allan, S. J. Clark, R. M. Ibberson, S. Parsons, C. R. Pulham and L. Sawyer, *Chem. Commun.*, 1999, 751-752.
6. M. Bujak, A. Budzianowski and A. Katrusiak, *Z. Kristallogr.*, 2004, **219**, 573-579.
7. J. Ridout and M. R. Probert, *Cryst. Growth Des.*, 2013, **13**, 1943-1948.
8. I. D. H. Oswald, D.R. Allan, W. D. S. Motherwell and S. Parsons, *Acta Crystallogr., Sect. B:Struct. Sci.*, 2005, **61**, 69-79.
9. R. Gajda, K. F. Dziubek and A. Katrusiak. *Acta Crystallogr. Sect. B: Struct. Sci.*, 2006, **62**, 86-93.
10. M. R. Probert, Y. H. P. Chung and J. A. K. Howard, *CrystEngComm*, 2010, **12**, 2584-2586.
11. A. R. Choudry, K. Islam, M. T. Kirchner, G. Mehta and T. N. Guru Row, *J. Am. Chem. Soc.*, 2004, **126**, 12274-12275.
12. A. M. Dikundwar, R. Sathiskumar, T. N. Guru Row and G. R. Desiraju, *Cryst. Growth Des.*, 2011, **11**, 3954-3963.
13. D. Chopra, V. Thiruvenkatam and T. N. Guru Row, *Cryst. Growth Des.*, 2006, **6**, 843-845.
14. A. J. Cruz-Cabeza, G. M. Day and W. Jones, *Chem. Eur. J.*, 2008, **14**, 8830-8836.
15. D. E. Braun, P. G. Karamertzanis and S. L. Price, *Chem. Commun.*,

2011, **47**, 5443-5445.
16. D. S. Yufit and J. A. K. Howard, *J. Appl. Crystallogr.*, 2012, **14**, 8222-8227.
17. G. J. Piermarini, S. Block, J. D. Barnett and R. J. Forman. *J. Appl. Phys.*, 1975, **46**, 2774-2780.
18. R. Boese and M. Nussbaumer. *Organic Crystal Chemistry*, Oxford University Press: Oxford, U.K., 1994.
19. M. R. Probert, J. A. Coome, A. E. Goeta and J. A. K. Howard, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2011, **67**, 528.
20. M. R. Probert, C. M. Robertson, J. A. Coome, J. A. K. Howard, B. C. Mitchell and A. E. Goeta, *J. Appl. Crystallogr.*, 2010, **43**, 1415-1418.
21. T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2009, **42**, 885-891
22. ECLIPSE, S. Parsons, The University of Edinburgh: Edinburgh, U. K. 2009.
23. SAINT, Bruker AXS Inc.: Madison, WI, 2007.
24. SADABS, Bruker AXS INC.: Madison, WI, 2001.
25. *APEX2*, version 1.08, Bruker AXS Inc.: Madison, WI, 2004.
26. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallog.*, 2008, **64**, 112.
27. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. J. Puschmann, *J. Appl. Crystallog.*, 2009, **42**, 339-341.
28. J. W. Steed, *CrystEngComm*, 2003, **5**, 169-179.
29. R. Taylor and C. F. Macrae, *Acta Crystallogr. Sect. B: Struct. Sci.*, 2001, **57**, 815-827.
30. D. R. Allan, S. J. Clark, M. J. P. Brugmans, G. J. Ackland and W. L. Vos, *Phys. Rev. B: Condens. Matter.*, 1998, **58**, 11809.
31. P. G. Jonsson, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1976, **32**, 232.