The influence of pressure and temperature on the crystal structure of acetone

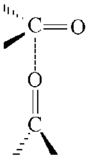
David R. Allan,[a] Stewart J. Clark,[b] Richard M. Ibberson,[c] Simon Parsons,[d] Colin R. Pulham[d] and Lindsay Sawyer[e]

[a] *Department of Physics and Astronomy, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland, UK EH9 3JZ*
[b] *Department of Physics, University of Durham, South Road, Durham, UK DH1 3LE*
[c] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK OX11 0QX*
[d] *Department of Chemistry, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland, UK EH9 3JJ. E-mail: s.parsons@ed.ac.uk*
[e] *Structural Biochemistry Group, ICMB, The University of Edinburgh, Michael Swann Building, King's Buildings, West Mains Road, Edinburgh, Scotland, UK EH9 3JR*

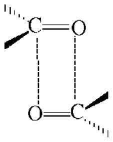
Received (in Cambridge, UK) 20th January 1999, Accepted 16th March 1999

Dipolar carbonyl–carbonyl contacts generally occur in one of three motifs, and all are exhibited in the X-ray crystal structures of two phases of acetone derived at 15 kBar and at 150 K; a neutron powder-diffraction study at 5 K and an X-ray diffraction study at 110 K reveal strengthened CH···O as well as CO···CO electrostatic contacts which appear to explain the unusual thermodynamic properties of acetone, the nature of which have remained a mystery since 1929.

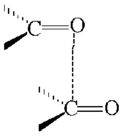
One motive for performing crystallographic studies on very simple systems is that they can reveal structural motifs that are applicable to whole classes of compound. Though there are few compounds so familiar in the laboratory as acetone, little is known about its structure in the solid state. We now describe five crystal structures of acetone determined at high pressure and at low temperature. The two distinct phases characterised in this study exhibit all three of the archetypal packing motifs identified in an important recent survey of dipolar carbonyl–carbonyl interactions.[1] The identification of more than eighty 'highly unsatisfied' main-chain H-bond acceptors in protein structures[2] reflects the likely structural significance of dipolar interactions in biological macromolecules,[3] and the results described here are relevant to identifying and modelling these contacts. We have also been able to suggest a solution to a long-standing question about the thermodynamic properties of crystalline acetone.[4,5]



Type I



Type II



Type III

A sample of acetone was solidified at room temperature under pressure and a single crystal obtained by the methods described in ref. 6. X-Ray diffraction data were collected at 15 kBar (at room temperature), and structure solution† revealed a C-centred orthorhombic phase composed of layers of acetone molecules disposed along the *c*-axis. The layers consist of molecules stacked along the [010] direction, in which each molecule is involved in four C···O contacts formed in a sheared-parallel motif (Type III, Fig. 1) with a $C{=}O\cdots C{=}O$ distance of 3.365(2) Å, which is slightly shorter than the median for this type of interaction (3.45 Å).[1]

An orthorhombic C-centred phase can also be obtained by cooling the liquid slowly through the melting point at ambient pressure. A data set acquired at 165 K showed this to be essentially isostructural with the high pressure phase, except that the cell dimensions increase by between 4 and 7%.‡ This phase is metastable and decomposes after a few hours to the primitive phase described below. The shortest 'Type III' $C{=}O\cdots C{=}O$ distance is 3.587(3) Å, and in the context of other, similar, interactions examined in ref. 1 this contact is of marginal significance. Since there do not appear to be any other notable contacts, this may explain the instability of this phase.

During the course of this study this metastable phase was observed only twice, and the precise conditions which promote its formation are as yet unclear, although it seems to decompose more quickly the lower the temperature. All other low-temperature crystallisations yielded a stable, primitive orthorhombic phase.§ Once again, the crystal structure (determined at 150 K) consists of layers of molecules stacked along the *c*-axis, which is approximately twice as long as in the high pressure phase because neighbouring layers are crystallographically independent. The arrangement of molecules in the layers is quite different from that observed at high pressure. In one layer [Fig. 2(*a*)] pairs of molecules interact in antiparallel fashion ['Type II', C···O 3.300(3) Å], with each pair forming perpendicular 'Type I' contacts to neighbouring molecules [C···O 3.491(3) Å]. The other layers [Fig. 2(b)] consist of chains of molecules interacting only *via* the perpendicular motif [C···O 3.458(3) Å]; the closest C to O distance between the chains is 3.74 Å.

Calorimetric studies on crystalline acetone show a broad peak in the heat capacity *vs.* temperature curve centred around 127 K. The origin of this behaviour has remained an unresolved issue since it was first observed in 1929,[4] although the entropy change suggested that it was not associated with an order–disorder transition or rotations of the methyl groups.[5] Neutron powder diffraction patterns were measured for acetone between 5 and 140 K, and at all temperatures these patterns could be indexed on primitive orthorhombic unit cells similar to that given in

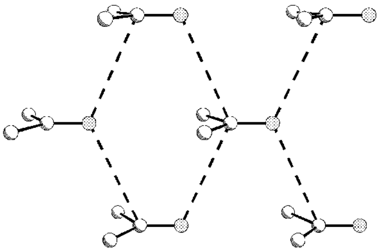


Fig. 1 Skew-parallel (Type III) $C{=}O\cdots C{=}O$ intermolecular interactions in the crystal structure of acetone at 15 kBar. H-atoms are disordered and omitted for clarity.

footnote §, although the cell dimensions changed rapidly and anisotropically with temperature. The crystal structure could not be resolved in the original neutron study, and so a firm statement regarding the structural nature of the heat capacity behaviour was not possible.[5]

We have refined the structure of acetone against the neutron powder data set collected at 5 K¶ to reveal C–H···O contacts of 2.336(6) and 2.479(5) Å respectively formed between and within the chains of molecules shown in Fig. 2(*b*); the angles at the donor H-atoms are 154.9(3) and 133.4(3)°. The dipolar contacts are also shorter at 5 K, and details are given in the figure captions. Although O···H distances derived from X-ray and neutron diffraction experiments are difficult to compare directly, at 150 K only one C–H···O contact (2.51 Å, where the C–H distance has been 'normalised' to 1.08 Å) falls within the sum of the van der Waals radii of O and H (2.60 Å).

It seemed plausible that the variation of heat capacity with temperature is associated with the strengthening of electrostatic C=O···C=O and CH···O contacts. This was confirmed in a variable-temperature X-ray structure determination study which at 110 K§ shows three contacts 'locking-in' with significantly shortened distances: the CH···O contact between the chains in Fig. 2(*b*) has an X-ray CH···O distance of 2.511(12) Å, compared to 2.618(13) Å at 150 K; the CH···O contact within the chains shortens from 2.71(2) to 2.604(18) Å, and the Type I (perpendicular) C=O···C=O interaction between the molecules in Fig. 2(*a*) shortens from 3.491(4) to 3.417(4) Å. The cell dimensions derived in this single crystal study are somewhat different from those obtained in the variable temperature neutron powder-diffraction study. It is important to emphasise that the heat capacity transition is very broad, occurring over a range of some 60 K, and varies with the thermal history of the sample.[5] Structural parameters observed in a particular run of experiments may well therefore exhibit effects which are sample-specific.

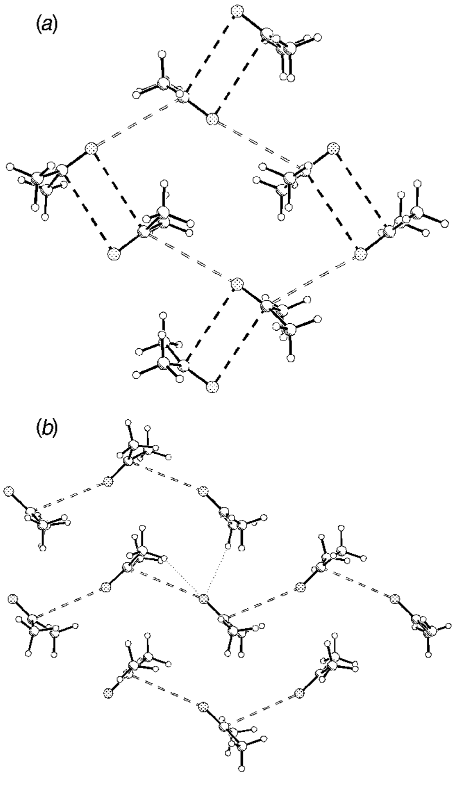


Fig. 2 The stable primitive orthorhombic phase of acetone at 150 K. (*a*) Layers containing perpendicular and antiparallel carbonyl interactions. The C···O distances at 5 K were 3.368(4) and 3.231(5) Å, respectively. (*b*) Layers comprised of strands of acetone molecules interacting *via* the perpendicular motif [Type I, 3.391(4) Å at 5 K]. Also shown (dotted lines) are C–H···O contacts that assume importance at 5 K.

A series of *ab initio* density functional calculations was performed with the aim of modelling the enthapy derived experimentally for this phase transition (259 J mol^{-1}).‖ Since the systems are periodic, an unbiased plane wave basis set was used to express the electronic wavefunction to alleviate the convergence problems of traditional quantum chemistry basis sets.[7] On minimising the total energy of the systems, the energy difference between the phases is 215 J mol^{-1}. This is below the experimental value because total energy calculations measure the absolute difference in the local energy minima of the two phases, and do not take dynamics into account.

We thank Mr Hugh Vass for technical assistance and the EPSRC for support.

Notes and references

All structures were solved by direct methods (ref. 8) and refined with Shelxl (ref. 9); *R* factors were between 5 and 6%.

† *Crystal data* for acetone at 15 kBar: C_2H_6O, M = 58.04, orthorhombic, a = 6.1219(11), b = 5.2029(10), c = 10.244(3) Å, *Cmcm*, Z = 4. The methyl groups are rotationally disordered about the C–C axis.

‡ *Crystal data* for the metastable C-centred orthorhombic low-temperature phase of acetone: a = 6.514(4) , b = 5.4159(18), c = 10.756(5) Å, U = 379.5(3) Å^3, T = 165 K, *Cmcm*. The H-atoms are ordered and were located in a difference map and refined freely.

§ *Crystal data* for the stable orthorhombic low-temperature phase of acetone: a = 8.873(3), b = 8.000(4), c = 22.027(7) Å, U = 1563.5(10) Å^{-3}, T = 150 K, *Pbca*, Z = 16, H-atom positional parameters were refined subject C–H and H–H similarity restraints. Cell dimensions at 110 K: a = 9.172(8), b = 7.761(8), c = 21.66(2) Å, U = 1542(3) Å^3.

¶ Time-of-flight diffraction data were recorded on the High Resolution Powder Diffractometer (ref. 10) at the ISIS spallation neutron source at 5 K over a time-of-flight range of 30 to 230 ms corresponding to a *d*-spacing range of 0.6 to 4.6 Å. a = 9.16686(1), b = 7.53231(1), c = 21.24861(5) Å. The structure was refined without constraints using the Rietveld method (ref. 11, 12) and using the 150 K structure as the starting model (space group *Pbca*). Only the D atoms were refined anisotropically. R_E = 1.64%, R_P = 3.03%, R_{wP} = 3.84%, χ^2 = 5.48 for 5948 observations and 162 basic variables. CCDC 182/1197. Crystallographic data are available in CIF format from the RSC web site, see: http://www.rsc.org/suppdata/cc/1999/751/

‖ The calculations were performed using the CASTEP density functional code (ref. 13). A generalised gradient approximation (ref. 14) was used to describe the exchange and correlation energy, requiring a plane wave basis set of 1.5 million functions for convergence. The *ab initio* forces on the atoms and stresses on the unit cell were used to perform an energy minimisation of the structure using a pre-conditioned conjugate gradients routine (note that these calculations refer to systems at zero-pressure and so the quantity minimised was the total energy of the system *U*). During the relaxation no symmetry constraints were applied; symmetry-breaking was not observed.

1 F. H. Allen, C. A. Baalham, J. P. M. Lommerse and P. R. Raithby, *Acta Crystallogr.*, 1998, **B54**, 320.
2 I. K. McDonald and J. M. Thornton, *J. Mol. Biol.*, 1994, **238**, 777.
3 P. H. McCallum, R. Poet and E. J. Milner-White, *J. Mol. Biol.*, 1995, **248**, 361 and 374.
4 K. K. Kelley, *J. Am. Chem. Soc.*, 1929, **51**, 1145.
5 R. M. Ibberson, W. I. F. David, O. Yamamuro, Y. Miyoshi, T. Matuso and H. Suga, *J. Phys. Chem.*, 1992, **99**, 14 167.
6 W. L. Vos, L. W. Finger, R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.*, 1993, **71**, 3150.
7 D. R. Allan, S. J. Clark, M. J. P. Brugmans, G. J. Ackland and W. L. Vos, *Phys. Rev. B*, 1998, **58**, 11 809.
8 A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
9 G. M. Sheldrick, Shelxl-97, University of Göttingen, 1997.
10 R. M. Ibberson, W. I. F. David and K. S. Knight, Rutherford Appleton Laboratory Report, RAL-92-031, 1992.
11 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
12 W. I. F. David, R. M. Ibberson and J. C. Matthewman, Rutherford Appleton Laboratory Report, RAL-92-032, 1992.
13 M. C. Payne, M. P. Teter, D. C. Allan and T. A. Arias, *Rev. Mod. Phys.*, 1992, **64**, 1045.
14 J. P. Perdew and Y. Wang, *Phys. Rev.*, 1992, **B46**, 6671.

Communication 9/00558G