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Migration of the proton in the strong O—H···O hydrogen bond in urea–phosphoric acid (1/1)

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The structure of urea–phosphoric acid is reported at a large number of temperatures in the range 150–335 K from neutron diffraction data collected using a novel multiple single-crystal data collection method. The work focuses on the behaviour of the H atom involved in the short strong O—H···O hydrogen bond in this material. The position of this atom is shown to vary significantly, by around 0.035 Å, as a function of temperature, becoming effectively centred at the highest temperatures studied. This result, only accessible due to the accurate determination of H-atom parameters by neutron diffraction, has implications for the potential governing the hydrogen bond.

1. Introduction

We have recently begun to quantify the possibilities for deliberately using multiple single-crystal samples to collect neutron diffraction data from low-symmetry molecular systems (Wilson, 1997*a*). There are several situations in which such an approach can be profitable. First, the use of a multiple crystal sample can lead to a reduction in data collection time – in the ideal case being reduced approximately in direct proportion to the number of crystals used. This facilitates, for example, more rapid scanning of a structure as a function of temperature. Second, if the samples are quasi-randomly aligned in the beam, it should be possible to obtain full three-dimensional diffraction data using very limited sample re-orientations; for example, rotation about a single axis may yield sufficient data for good structural refinement. Thirdly, in the case where only small crystals can be grown, but several of these may be available, the method may make structure determination feasible.

Previous experiments which have used multiple crystal samples have tended to aim towards creating a composite sample of closely aligned individual crystals, particularly of high-symmetry systems, or have been carried out 'accidentally' on twinned or clustered crystals (Tichý *et al.*, 1980; Gao *et al.*, 1994). A previous quantification of multiple crystal data collection techniques inside complex sample environment apparatus was successful in developing algorithms for indexing multiple crystal diffraction patterns (Johnson *et al.*, 1993). In this previous work no fewer than seven crystals were present in the sample, all of which were successfully indexed. However, it was not possible to refine the structure due to severe peak overlap between the patterns. The novel aspect of our work in this area is to *deliberately* use multiple single crystals of a low-symmetry system as a controlled part of the experiment design, and hence to allow for more efficient separation of peaks from the individual crystals. We have

Table 1
Summary of data collection and refinement parameters.

Diffractometer	SXD neutron time-of-flight Laue diffractometer											
Detectors	Two, 64 × 64 element, 3 × 3 mm pixel, scintillator PSDs											
Detector position	Low angle: $2\theta_c = 55°$, $L_2 = 188$ mm; high-angle: $2\theta_c = 125°$, $L_2 = 158$ mm											
Wavelength range (Å)	0.5–5.0											
Compound	Urea–phosphoric acid (1/1), $C(NH_2)_2OH\cdot PO_2(OH)_2$; $CH_7N_2O_5P$											
Molecular Weight	158.05											
Recrystallizing solvent	Aqueous											
Crystal size	5–15 mm^3 (three crystals used simultaneously for data collection)											
Unit cell	Space group *Pbca*, $Z = 8$											
T (K)	150–335											
a (Å)	17.42–17.65 (typical e.s.d.'s 0.009–0.015)											
b (Å)	7.42–7.47 (typical e.s.d.'s 0.002–0.003)											
c (Å)	8.94–8.98 (typical e.s.d.'s 0.002–0.003)											
V (Å^3)	1158–1184											
$\rho_{\rm calc}$ (g cm^{-3})	1.812–1.828											
Data collection												
T (K)	150	250	280	290	295	300	305	310	315	320	330	335
Observed reflections	2327	1798	2087	2010	1928	1858	1817	1804	1756	1694	1661	1395
Unique reflections $I > 3\sigma(I)$	1037	782	705	686	677	649	645	636	617	594	606	553
$R_{\rm int}$	0.079	0.066	0.087	0.071	0.074	0.074	0.066	0.066	0.069	0.070	0.075	0.084
Total data collection time (mins)	200	300	350	350	350	350	350	350	350	350	450	450
Absorption coefficient, μ (cm^{-1})	$1.00 + 0.96\lambda$											
Refinement												
Refinement	In *GSAS*, refined on F^2, $w = 1/[\sigma(F_o^2)]^2$ weights											
Refined parameters	145, all atoms anisotropic, including H atoms											
T (K)	150	250	280	290	295	300	305	310	315	320	330	335
$R(F)$	0.103	0.093	0.121	0.097	0.094	0.090	0.099	0.101	0.102	0.103	0.101	0.102
$wR(F^2)$	0.185	0.171	0.191	0.159	0.163	0.154	0.165	0.167	0.166	0.161	0.163	0.177

shown this to be a highly effective method for collecting good quality data from molecular structures (Wilson, 1997*a*).

The possibilities of collecting such multiple crystal data sets are enhanced by the use of the time-of-flight Laue data collection method. This method, implemented on the SXD diffractometer at the ISIS spallation neutron source (Wilson, 1990, 1997*b*), allows for fully resolved three-dimensional data volumes to be accessed in a single measurement (a frame) from a stationary crystal-detector arrangement. The three-dimensional nature of the data thus gives the best possible chance of avoiding accidental overlap from reflections from the different crystals in the sample, since these can be separated in both space and time-of-flight (≡ wavelength) on the detector.

Since the method has been developed for neutron diffraction data, our focus is on examining H-atom parameters. These are ideally studied using the technique, due to the fact that hydrogen parameters are determined with approximately the same precision as those for the other atoms in a neutron study. The accurate determination of H-atom positional and anisotropic displacement parameters can often show that there is much of interest happening with these atoms, even in apparently 'normal' crystal structures. The structure of urea–phosphoric acid, reported here, is an excellent example of the presence of this type of interesting-atom behaviour. In this case the focus is on the atom in the short, strong O—H···O hydrogen bond linking the two moieties in the complex (O···O distance ~2.41 Å; see Fig. 1).

Urea has been widely used as a complexing agent for organic acids in investigations of hydrogen-bonding phenomena. In the example studied here, urea–phosphoric acid (1/1), the complex displays a degree of H-atom transfer intermediate between complete (salt formation) and almost nil (addition complex formation). We can use the hydrogen-bond 'asymmetry', Δ, to characterize this, Δ being defined as the difference between the non-bonded H···O and bonded O—H distances. Previous neutron diffraction measurements have indicated that the partially transferred proton in the title complex at room temperature (Δ = 0.016 Å) has a thermal ellipsoid indicative of potential disordering across two sites (Kostansek & Busing, 1972), while the structure determined by neutron diffraction at 100 K showed the proton clearly to occupy a more asymmetric position within the hydrogen bond at low temperature, with Δ = 0.088 Å (Harkema, 1993) and to have a less elongated thermal ellipsoid. However, as is usually the case in such short hydrogen bonds, the covalent O—H distance is considerably lengthened, even in the more asymmetric situation at low temperature [O5—H4 distance of 1.163 (9) Å at 100 K]. To investigate this further, we recently performed a conventional variable-temperature single-crystal neutron diffraction study to examine the structure of urea–phosphoric acid at a range of temperatures between 150 and 350 K (Wilson *et al.*, 2001) with the express aim of determining any change in the position, thermal vibrations or occupancy of the H atom involved in the short hydrogen bond.

In this recent variable-temperature neutron work refinements of the structure were carried out using a single proton site model, showing that the proton appears to migrate along the bond as the temperature increases (Wilson *et al.*, 2001). The asymmetry of the proton position reduces from Δ ≃

0.07 Å at 150 K to approximately zero above 300 K. However, the temperature steps used in this related study are also necessarily coarse (25–50 K) and the study of this phenomenon would clearly benefit from further data in this temperature range. Only the multiple crystal method will allow sufficient data to allow precise refinements to be obtained from short data collection times and thus allow the temperature dependence of the structure to be studied in sufficient detail in the temperature range around 300 K. We report here neutron diffraction studies of the urea–phosphoric acid structure at 150, 250 and between 280 and 335 K in temperature steps of 5–10 K, using our multiple single-crystal method of data collection.

2. Experimental

A four-crystal sample of the title compound was mounted in a vertical stack inside a closed-cycle refrigerator on the SXD time-of-flight Laue diffractometer at the ISIS spallation neutron source (Wilson, 1990, 1997*b*). The individual sample volumes were in the range 5–15 mm^3. The overall vertical extent of the multiple-crystal stack was around 14 mm and a nominal 15 mm diameter incident beam was used for the experiment. The orientation matrices for each crystal were obtained using the procedure described previously (Wilson, 1997*a*). It was found that one of the four crystals was mounted so as to scatter only very weakly, in fact sitting just below the main neutron beam flux, and so quantitative data were only collected from three of the crystals in the stack. Determination of the three **UB** matrices from these confirmed that the desired fairly random alignment of the crystals relative to each other had been obtained, thus promising to yield the desired full three-dimensional diffraction data from the limited (ω-only) rotation accessible in the cooling device used. Data collection proceeded from the stack of crystals, with the diffraction measured in an array of two position-sensitive detectors located at different scattering angles around the sample position. With three crystals diffracting simultaneously into the two PSDs, it was found possible to collect a fairly representative set of diffraction data in just three or four crystal orientations ('frames') – a very favourable set-up for the intended rapid scanning variable-temperature experiment.

Data were collected at 14 temperatures between 150 and 335 K, with frame times of between 1 and 2 h per crystal position, yielding typical total data collection times of around 5–6 h at each temperature. There was evidence of significant temperature fluctuations during collection of the data sets at 270 and 325 K, and these were omitted. This was due to an intermittent heater fault, which temperature logging confirmed did not affect the data at the other temperature points. The data at the remaining temperatures were processed using standard SXD procedures, with the added check that any reflection potentially arising from scattering by more than one of the four crystals in the stack (including the weakly scattering out-of-beam crystal) was eliminated from the data set prior to merging. This resulted in reasonable

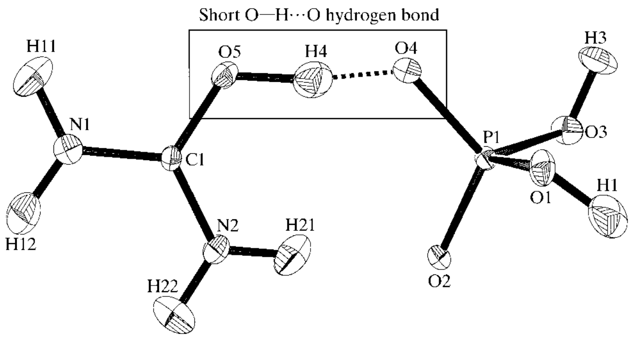

Figure 1
*ORTEP*II (Johnson, 1971) plot of the urea–phosphoric acid structure at 150 K, showing the atomic numbering and the strong O—H···O hydrogen bond. Note that partial transfer of the H atom (elongation of O5—H4) is indicative of the significant formation of the salt uronium phosphate. Probability ellipsoids are drawn at the 50% level.

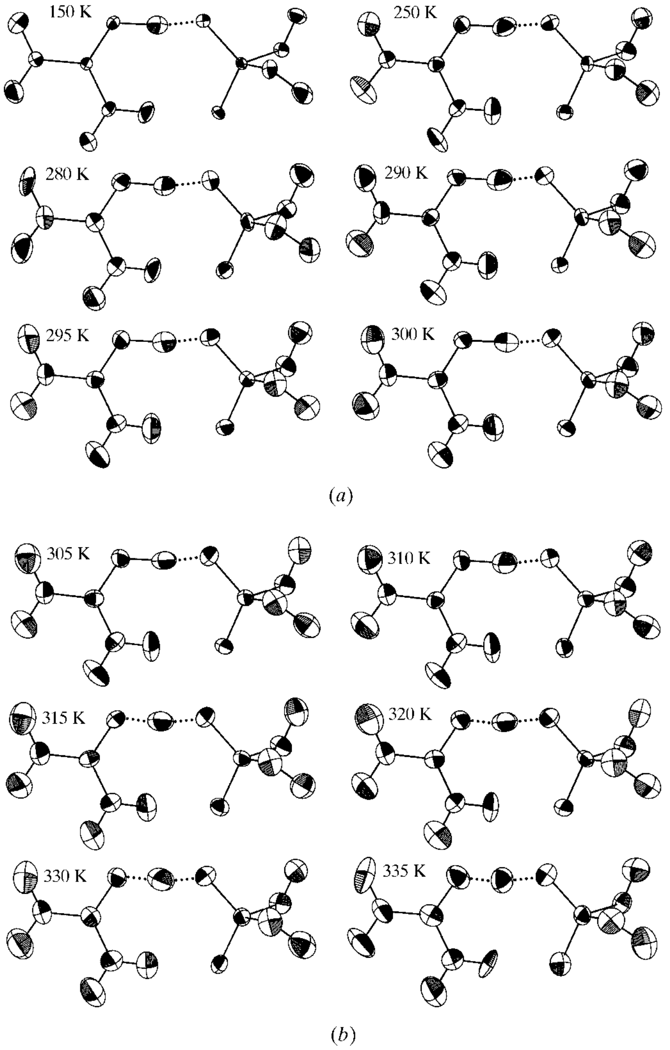

Figure 2
The evolution of the urea–phosphoric acid structure as a function of temperature between 150 and 335 K (drawn using *ORTEP*II, Johnson, 1971, with 50% probability ellipsoids). The significant migration of the proton in the short strong hydrogen bond is emphasized by our choice of covalent bond limits for O—H bonds in these plots – at 315 K and above the H atom has moved sufficiently close to the midpoint of the O···O vector so as not to appear bonded to either in these plots.

Table 2
Urea–phosphoric acid, multiple-crystal experiment: hydrogen-bond geometries.

The geometry of the short O4—H4···O5 'intramolecular' hydrogen bond and the normal (O1—H1···O2 [O2′ $(\frac{1}{2}-x, y-\frac{1}{2}, z)$] and O3—H3···O2 [O2″ $(x, \frac{1}{2}-y, z-\frac{1}{2})$]) intermolecular hydrogen bonds. The hydrogen bond angles in the former vary from 166 to 171° and the latter are effectively straight, with O—H···O angles in the range 175–178°.

Distance	150 K	250 K	280 K	290 K	295 K	300 K	305 K	310 K	315 K	320 K	330 K	335 K
O1···O2	2.642 (6)	2.648 (7)	2.669 (10)	2.659 (8)	2.665 (9)	2.661 (8)	2.651 (10)	2.656 (9)	2.696 (9)	2.695 (10)	2.676 (10)	2.687 (12)
O1—H1	0.985 (10)	0.974 (12)	1.003 (14)	0.960 (16)	0.994 (14)	0.971 (14)	0.964 (17)	0.977 (17)	1.014 (15)	1.015 (17)	0.994 (18)	1.012 (22)
H1···O2	1.658 (9)	1.676 (11)	1.668 (12)	1.702 (13)	1.677 (12)	1.693 (12)	1.690 (14)	1.682 (14)	1.686 (12)	1.684 (13)	1.685 (14)	1.679 (17)
O3···O2	2.568 (5)	2.575 (6)	2.593 (6)	2.573 (5)	2.580 (6)	2.562 (6)	2.570 (6)	2.568 (7)	2.571 (7)	2.561 (7)	2.568 (7)	2.554 (8)
O3—H3	1.008 (7)	1.003 (9)	1.032 (12)	1.030 (10)	1.016 (11)	1.016 (10)	1.033 (13)	1.024 (14)	1.038 (13)	1.016 (16)	1.002 (12)	0.988 (16)
H3···O2	1.561 (7)	1.573 (8)	1.563 (10)	1.545 (8)	1.566 (9)	1.547 (9)	1.540 (11)	1.546 (11)	1.534 (11)	1.546 (13)	1.567 (10)	1.570 (12)
O4···H4	1.231 (8)	1.237 (9)	1.240 (11)	1.235 (10)	1.252 (10)	1.238 (10)	1.231 (10)	1.239 (10)	1.219 (11)	1.222 (11)	1.221 (12)	1.226 (13)
O5···H4	1.178 (8)	1.176 (10)	1.195 (12)	1.179 (11)	1.180 (11)	1.193 (11)	1.199 (11)	1.201 (11)	1.221 (11)	1.214 (12)	1.208 (13)	1.214 (15)
O4···O5	2.400 (5)	2.405 (6)	2.417 (7)	2.403 (6)	2.420 (7)	2.422 (6)	2.422 (7)	2.431 (7)	2.433 (7)	2.425 (8)	2.419 (8)	2.430 (9)

quality merged data sets at each temperature from which fully anisotropic refinements could be carried out. Although the data/parameter ratios are rather lower than ideal, the main aim of this work was to collect many temperature points to examine trends, rather than to aim for fuller data sets at individual temperatures. The data collection parameters are summarized in Table 1.

The structure was refined at each temperature using the program *GSAS* (Larson & Von Dreele, 1994), with the 150 K model from our conventional neutron study being used as a starting point for the refinement at 150 K, and the refined model at each temperature being used in turn as the starting point for the refinement at the succeeding temperature. The pattern of standard uncertainties on the fractional coordinates, and the quite normal appearance and refined characteristics of the anisotropic atomic displacement parameters on all the atoms in the structure (Fig. 2), confirmed the representative three-dimensional nature of the data sets collected in the vertical geometry employed. The fact that so many data sets can be collected from a low-symmetry organic structure in just 3 d in a neutron single-crystal experiment offers considerable promise for future opportunities with this technique.

3. Results and discussion

The refined coordinates, bond lengths and angles are given in the supplementary material,[1] but it is not upon the full description of the structure that we focus here. The aim of the experiment is to examine, as a detailed function of temperature, the geometry and specifically the H-atom location in the short, strong hydrogen bond in the title compound. The well behaved nature of the other atomic parameters in the refined structures in this sense merely lends support to our conclusions on this important point.

The geometry in this hydrogen bond is summarized in Table 2. It can be clearly seen that, within the scatter of points expected from an experiment like this using very rapid (for neutron diffraction) structure determinations, the position found for the H atom does vary in a systematic way as the temperature increases. This is most strikingly illustrated in Fig. 3, which shows the two O—H distances in this hydrogen bond as a function of temperature. These two distances clearly become more equal – the H atom migrates towards the midpoint of the O···O separation, with the hydrogen bond effectively becoming more centred as the temperature increases to 300 K and beyond. This is a striking result, with interesting implications for possible temperature-dependent variations in the shape of the hydrogen-bond potential in this, and other, strongly hydrogen-bonded system. Clearly the migration of the proton is smooth, but although a guide to the eye is drawn in Fig. 3 to emphasize this, there is no obvious simple thermodynamic model for this movement. From the evidence seen here, it seems most likely to reflect subtle changes in the shape of the potential due to slight changes in the local environment with temperature. In passing, it is worth noting that a very simple bond-valence interpretation of this

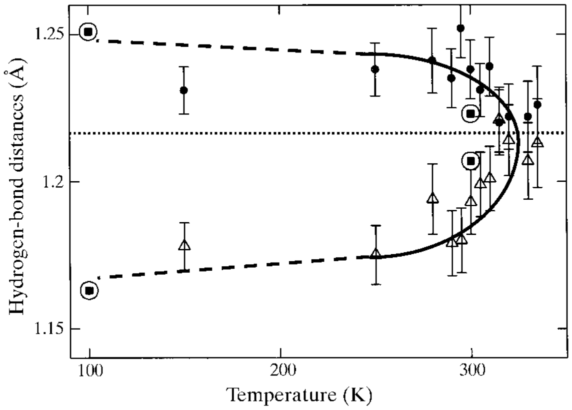

Figure 3
The increasingly symmetric location of the proton in the short, strong hydrogen bond in urea–phosphoric acid is illustrated by the convergence of the 'bonded' (O5–H4; open triangles) and non-bonded (H4···O4; filled circles) distances as the temperature increases. Also shown on this plot (as filled squares inside circles – error bars omitted for clarity) are the values found by Harkema (1993) at 100 K (unpublished work) and by Kostansek & Busing (1972) at room temperature (assumed to be around 300 K). The lines are a guide to the eye and the dotted line indicates the 'centred' situation found here above ~300 K.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0570). Services for accessing these data are described at the back of the journal.

situation is fairly enlightening (Brown, 1982). This analysis shows that both interatomic interactions in this hydrogen bond are sufficiently long as to be in the flat region in the empirical bond-valence curves, resulting in little variation in the bond-valence sum as the temperature changes. This provides further evidence that there is little thermodynamic penalty associated with changing the position of the proton in this hydrogen bond, as observed here and points towards the more subtle potential shape effects alluded to above. The confirmation of this effect is only really made possible by the rapid scanning multiple-crystal method employed here. As expected, there is some elongation of the H-atom thermal ellipsoid at the higher temperatures studied, in agreement with the findings of Kostansek & Busing (1972), but the quality of our data are not sufficient to allow this to be investigated further.

We can contrast the situation in the short O···O hydrogen bond with that in the more conventional O1—H1···O2 and O3—H3···O2 intermolecular hydrogen bonds in the same structure (Table 2). In the latter, the only significant trend with increasing temperature is a slight increase in the non-bonded H1···O2 distance following expansion of the unit cell.

4. Conclusions

We have used our recently developed novel multiple-crystal data collection method to show that the H-atom position in the short, strong hydrogen bond in urea–phosphoric acid alters significantly as a function of temperature. The H atom 'migrates' towards the mid-point of the hydrogen bond as the temperature is increased, becoming essentially centred at $T >$ 300 K. This is a significant observation, made possible only by measuring the structure at a range of temperatures. Variable-temperature experiments are thus once again seen to add information to that available from even the best single-temperature high-resolution measurements. It is clear that the result presented in Fig. 3 is most compelling due to the large number of temperature points accessed, only possible using novel data collection methods such as that employed here.

The urea–phosphoric acid samples used in this work were cut from a large single crystal grown by Dr N. Shankland and Dr A. J. Florence at the University of Strathclyde. This work was funded by EPSRC under grant GR/M41773.

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